Publication number:

0068813

12

#### **EUROPEAN PATENT APPLICATION**

- Application number: 82303281.8
- Date of filing: 23.06.82

Int. CL3: C 07 F 7/08, C 07 F 7/18, A 01 N 55/00

Priority: 24.06.81 US 276986 16.02.82 US 349261 12.05.82 US 377122

24.06.81 US 276987 16.02.82 US 349262 12.05.82 US 377121 Applicant: E.L DU PONT DE NEMOURS AND COMPANY, Legal Department 1007 Market Street, Wilmington Delaware 19898 (US)

Date of publication of application: 05.01.83 Bulletin 83/1

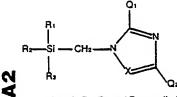
Inventor: Moberg, William Karl, 1921 Kynwyd Road, Wilmington Delaware 19810 (US)

Designated Contracting States: AT BE CH DE FR GB IT LILUNLSE

Representative: Hildyard, Edward Martin et al, Frank B. Dehn & Co. European Patent Attorneys Imperial House 15-19 Kingsway, London WC2B 6UZ (GB)

Fungicidal 1,2,4-triazole and imidazole derivatives.

1,2,4-Triazole and imidazole derivatives of the general formula



wherein  $R_1$ ,  $R_2$  and  $R_3$  are alkyl, naphthyl or optionally substituted phenyl; or  $R_2$  and  $R_3$  may be hydroxy or alkoxy; X is N, CH or CCH3; and

Q<sub>1</sub> and Q<sub>2</sub> are H or CH<sub>3</sub>;

are effective fungicides for controlling fungi in a plant locus. They may be formulated for use in conventional manner.

The compounds may be made e.g. by reacting a suitable chloromethylsilane with a suitable imidazole or 1,2,4-triazole. 1

Title BA-8453-B (Cognate)

# FUNGICIDAL 1,2,4-TRIAZOLE AND IMIDAZOLE DERIVATIVES

### Background of the Invention

The present invention relates to silylmethyltriazoles and imidazoles such as, for example, dimethyl(phenyl)(1H-1,2,4-triazol-1-ylmethyl)silane and
(1,1'-biphenyl-4-yl)dimethyl(1H-imidazol-1-ylmethyl)silane, and to the use of these new compounds, in controlling fungus diseases, particularly diseases of
living plants.

U.S. Patent 3,692,798 discloses compounds of the formula:

wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can be lower alkyl and phenyl.

It is stated that these compounds are useful as antimicrobial agents.

European Patent 29,993 discloses compounds of the formula:

$$\begin{array}{c|c}
 & 0 \\
 & N \\
 & N \\
 & Z
\end{array}$$

wherein R can be  $C_1$ - $C_4$  alkyl and Y and Z can be H or  $SiR_1R_2R_3$ , wherein  $R_1$ ,  $R_2$ , and  $R_3$  can be alkyl, haloalkyl, alkenyl, alkynyl, or substituted phenyl. It is taught that the compounds are useful as agricultural fungicides.

5

U.S. Patents 3,256,308 and 3,337,598 disclose compounds of the formula:

5

10

20

30

wherein  $R_1$  can be methyl, ethyl, vinyl, or phenyl. Their use to control fungi is also taught.

Belgian Patent 785,127 discloses quaternary ammonium salts such as:

$$_{(CH_{3}O)_{3}SiCH_{2}CH_{2}\overset{C}{h}-\underline{n}-C_{18}^{H_{37}}}^{CH_{3}}$$

and their use as fungicides. Research Disclosure 17,652 discloses silyl ethers of the formula:

wherein Ar can be substituted phenyl, X can be CH or N, and R can be alkyl. It is taught that the compounds are useful as agricultural fungicides.

West German Patent DE 3,000,140 discloses silyl ethers of the formula:

wherein Ar can be substituted phenyl, X can be CH or N, and R can be phenyl or lower alkyl. It is taught that these compounds are useful as agricultural fungicides.

U.S. Patent 4,248,992 discloses a class of organosilicon compounds having in a molecule at least one monovalent guanidine group represented by the general formula:

-N NR<sub>2</sub>

in which R is a hydrocarbon atom or a monovalent hylo drocarbon group. These guanidine-containing organosilicon compounds are described as useful as antifungal agents for molded plastics and rubbers,
particularly silicone rubbers.

U.S.S.R. Patent 346,306 discloses silylmethyl-15 azoles of the formula:

$$(R_1)_n(R_20)_{3-n}SICH_2Az$$

wherein  $\rm R_1$  and  $\rm R_2$  are alkyl groups, n is 0-3, and Az is a pyrazole, imidazole, or benzimidazole ring, optionally substituted.

U.S.S.R. Patent 271,552 discloses silylethylazoles of the formula:

$${\rm (R_1)_n(R_20)_{3-n}SiCH_2CH_2Az}$$

wherein  $R_1$ ,  $R_2$ , n, and Az are as described in the previous reference.

# Summary of the Invention

This invention relates to silylmethyltriazoles of Formula I and to silylmethylimidazoles of Formula II and to agriculturally useful compositions of these 5 compounds.

$$R_{2} = \frac{\overset{\overset{\circ}{\text{N}}_{1}}{\overset{\circ}{\text{N}}_{1}}}{\overset{\overset{\circ}{\text{N}}_{1}}{\overset{\circ}{\text{N}}_{1}}} = \frac{\overset{\overset{\circ}{\text{N}}_{1}}{\overset{\circ}{\text{N}}_{1}}}{\overset{\overset{\circ}{\text{N}}_{1}}{\overset{\circ}{\text{N}}_{1}}} = \frac{\overset{\overset{\circ}{\text{N}}_{1}}{\overset{\circ}{\text{N}}_{1}}}{\overset{\overset{\circ}{\text{N}}_{1}}{\overset{\circ}{\text{N}}_{1}}} = \frac{\overset{\circ}{\text{N}}_{1}}{\overset{\circ}{\text{N}}_{1}} = \frac{\overset{\circ}{\text{N}}_{$$

wherein

 $\mathbb{Q}_1$ ,  $\mathbb{Q}_2$  and  $\mathbb{Q}_3$  are independently H or  $\mathrm{CH}_3$ ; n is 1;

R<sub>1</sub> is C<sub>2</sub>-C<sub>18</sub> alkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, naphthyl, or

20

10

15

R'<sub>1</sub> is  $C_6-C_{18}$  alkyl,  $C_3-C_6$  cycloalkyl, naphthyl or

25

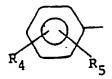
30

35

where

 $R_4$  and  $R_5$  are independently -H; halogen;  $-0CH_3$ ;  $-0CF_3$ ;  $-SCH_3$ ;  $-SO_2CH_3$ ; phenyl; phenyl substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or - $CF_3$ ; phenoxy; phenoxy substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or - $CF_3$ ; - $CF_3$ ;  $C_1$ - $C_4$  alkyl; or cyclohexyl; with the proviso that for compounds of Formula II, both  $R_4$  and  $R_5$  may not simultaneously be H; and

 $R_2$  and  $R_3$  are independently  $C_1$ - $C_6$  alkyl,  $C_3$ - $C_6$  cycloalkyl,  $OR_6$ , or



where  $R_4$  and  $R_5$  are as defined above except. that said proviso does not apply, and  $R_6$  is H or  $C_1$ - $C_4$  alkyl, with the proviso that both  $R_2$  and  $R_3$  may not be OH; and  $R_2$  and  $R_3$  together may be a 1,2- or 1,3- or 1,4-glycol bridge or a 1,4 unsaturated glycol bridge substituted by up to four alkyl groups  $R_7$ - $R_{10}$  that have a total of up to four carbon atoms.

$$R_7^{-R_{10}}$$
 or  $R_7^{-R_{10}}$  or  $R_7^{-R_{10}}$  or  $R_7^{-R_{10}}$ 

This invention also relates to a method for controlling fungus diseases, particularly fungus diseases
of living plants which comprises applying to the locus
to be protected an effective amount of a compound of
formula I or formula II

20 wherein

5

10

 $Q_1$ ,  $Q_2$  and  $Q_3$  are independently H or  $CH_3$ ; n is 1;

 $R_1$  and  $R'_1$  are  $C_2$ - $C_{18}$  alkyl,  $C_3$ - $C_6$  cycloalkyl, naphthyl, or

5

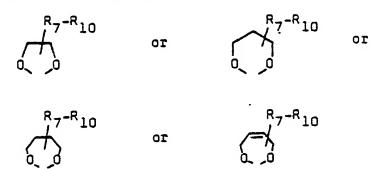
10

15

where

 $R_4$  and  $R_5$  are independently -H; halogen; -OCH $_3$ ; -OCF $_3$ ; -SCH $_3$ ; -SO $_2$ CH $_3$ ; phenyl; phenyl substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or -CF $_3$ ; phenoxy; phenoxy substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or -CF $_3$ ; -CF $_3$ ;  $C_1$ - $C_4$  alkyl; or cyclohexyl;  $R_2$  and  $R_3$  are independently  $C_1$ - $C_6$  alkyl,  $C_3$ - $C_6$  cycloalkyl,  $OR_6$ , or

where R<sub>6</sub> is H or C<sub>1</sub>-C<sub>4</sub> alkyl,
with the proviso that both R<sub>2</sub> and R<sub>3</sub> may not
be OH; and R<sub>2</sub> and R<sub>3</sub> together may be a
1,2- or 1,3- or 1,4-glycol bridge or a 1,4
unsaturated glycol bridge substituted by up to
four alkyl groups R<sub>7</sub>-R<sub>10</sub> that have a total
of up to four carbon atoms.



35

When  ${\bf R_2}$  or  ${\bf R_3}$  is OH, Formula I and Formula II are understood to include the disiloxane:

10 This invention also relates to salts of compounds of Formula I and Formula II with protic acids and complexes with metal ions.

Preferred for their high activity and/or favorable ease of synthesis are compounds of the generic scope wherein

 $Q_1 = Q_2 = H.$ 

More preferred for their higher activity and/or more favorable ease of synthesis are compounds of the preferred scope wherein

 $R_1$  and  $R_1^*$  are  $R_4$ ; and

 $R_2$  is  $C_1$ - $C_4$  alkyl or

15  $R_4$   $R_5$ ; and

 $R_3$  is  $C_1-C_4$  alkyl.

Most preferred for their highest activity and/or most favorable ease of synthesis are compounds of the more preferred scope wherein

$$R_1$$
 and  $R_1'$  are  $R_4$   $R_5$ ;

25 where

30

5

10

 $R_4$  is at the para position of  $R_1$  or  $R'_1$ , and  $R_4$  is H, F, Cl, Br, or phenyl, and

 $R_5$  is H, F, Cl. or Br; and  $R_2$  is

or  $C_1-C_4$  alkyl; and  $R_3$  is  $C_1-C_4$  alkyl.

```
Specifically preferred for their excellent
   activity and/or most favorable ease of synthesis are
   the following compounds of Formula I:
  ·(Dimethyl)phenyl(1H-1,2,4-triazol-1-ylmethyl)silane;
5 Dimethyl(4-methylphenyl)(1H-1,2,4-triazol-1-ylmethyl)-
   (4-Bromophenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)-
     silane;
   (1,1'-Biphenyl-4-y1)dimethyl(1H-1,2,4-triazol-1-y1-
     methyl)silane;
10
   (4-Chlorophenyl)dimethyl(lH-1,2,4-triazol-1-yl-
     methyl)silane;
    (2,4-Dichlorophenyl)dimethyl(lH-1,2,4-triazol-1-yl-
     methyl)silane;
15 Butyl(4-chlorophenyl)methyl(1H-1,2,4-triazol-1-yl-
      methyl)silane;
    bis(4-Chlorophenyl)methyl(1H-1,2,4-triazol-1-yl-
      methyl)silane;
    Methyl(diphenyl)(1H-1,2,4-triazol-1-ylmethyl)silane;
20 [bis(4-Fluorophenyl)]methyl(lH-1,2,4-triazol-1-yl-
      methyl)silane;
    (4-Fluorophenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)-
      silane;
    Butyl(2,4-dichlorophenyl)methyl(1H-1,2,4-triazol-1-yl-
      methyl)silane;
25
    [bis(2,4-Dichlorophenyl)]methyl(1H-1,2,4-triazol-1-yl-
      methyl)silane;
    2,4-Dichlorophenyl(methyl)phenyl(lH-1,2,4-triazol-1-yl-
      methyl)silane;
   4-Chlorophenyl(methyl)phenyl(lH-1,2,4-triazol-1-yl-
      me.thyl)silane;
    4-Fluorophenyl(methyl)phenyl(1H-1,2,4-triazol-1-yl-
      methyl)silane;
    Butvl(methyl)phenyl(lH-1,2,4-triazol-1-ylmethyl)silane;
35 Butyl(4-fluorophenyl)methyl(1H-1,2,4-triazol-1-yl-
      methyl)silane;
```

```
[bis(1,1'-Biphenyl-4-yl)]methyl(lH-1,2,4-triazol-1-yl-
methyl)silane;
```

- (1,1'-8iphenyl-4-yl)butyl(methyl)(lH-1,2,4-triazol-l-ylmethyl)silane; and
- 5 (1,1'-Biphenyl-4-yl)methyl(phenyl)(lH-1,2,4-triazol-1-ylmethyl)silane.

Especially preferred compounds, methods, and compositions of Formula II are those compounds wherein at least one group  $R_1$ ,  $R_2$  or  $R_3$  is other than lower

- 10 alkyl (C<sub>1</sub>-C<sub>4</sub>) or phenyl. In particular, the following compounds of Formula II are specifically preferred for their excellent activity and/or most favorable ease of synthesis:
  - (1,1'-Biphenyl-4-yl)dimethyl(lH-imidazol-1-ylmethyl)-
- 15 silane; (2,4-Dichlorophenyl)dimethyl(lH-imidazol-l-ylmethyl)-
  - Butyl(2,4-dichlorophenyl)(lH-imidazol-l-ylmethyl)methylsilane;
- 20 [bis(4-Fluorophenyl)](lH-imidazol-l-ylmethyl)methylsilane;
  - [bis(2,4-Dichlorophenyl)](lH-imidazol-l-ylmethyl)methylsilane;
  - (2,4-Dichlorophenyl)(lH-imidazol-l-ylmethyl)methyl (phenyl)silane;
  - (4-Chlorophenyl)(lH-imidazol-l-ylmethyl)methyl(phenyl)-silane:
  - (4-Fluorophenyl)(lH-imidazol-l-ylmethyl)methyl(phenyl)silane;
- 30 (1,1'-Biphenyl-4-yl)butyl(lH-imidazol-l-ylmethyl)methylsilane;
  - (1,1'-Biphenyl-4-y1)(lH-imidazol-1-ylmethyl)methyl (phenyl)silane;
- [bis(1,1-Biphenyl-4-yl)](1H-imidazol-1-ylmethyl)methylsilane;

Butyl(4-chlorophenyl)(lH-imidazol-l-ylmethyl)methylsilane;

(4-Chlorophenyl)dimethyl(lH-imidazol-l-ylmethyl)silane;

5 Dimethyl(4-fluorophenyl)(lH-imidazol-1-ylmethyl) silane; and

Butyl(4-fluorophenyl)(lH-imidazol-l-ylmethyl)methyl-silane.

When  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$  are both H or both  $\mathbf{CH}_3$ , the pro- 10 cess for preparing the triazole derivatives of Formula I will ordinarily produce a mixture of two triazole isomers:

15 
$$R_2 - Si - CH_2 - N_N = Q_2$$
 and  $R_2 - Si - CH_2 - N_N = Q_2$ 

Formula IA

Formula IB

Three isomers are possible when one triazole substituent is H and the other is CH3:

25 
$$R_2$$
- $Si$ - $CH_2$ - $N$  and  $R_2$ - $Si$ - $CH_2$ - $N$   $N$   $CH_3$ 

Formula IC

Formula ID

and 
$$R_{2} = \frac{R_{1}}{R_{3}} = CH_{2} - N$$

35

Formula IE

The mixture will contain predominately the isomers of Formula IA or Formula IC; however, the isomers of Formulae IB, ID, and IE also have fungicidal activity, and separation of the isomers is not required.

For the imidazole derivatives of Formula II, isomers are produced when  ${\bf Q}_2$  and  ${\bf Q}_3$  are not the same:

Formula IIA

Formula IIB

The isomers of Formula IIA will generally predominate; however, the isomer of Formula IIB also has fungitoxic activity and separation of the isomers is not required.

# Detailed Description of the Invention

In the following discussion,  $R_1$  is understood to represent both  $R_1$  and  $R_1$ ', since all values of  $R_1$ ' are included in the definition of  $R_1$ . Further, the term "azole" will be used to refer to appropriately substituted 1,2,4-triazoles and imidazoles

where  $Q_1$ ,  $Q_2$  and  $Q_3$  may be H or  $CH_3$ . In drawing structural formulas, the part-structure

35

where X is N or  $CQ_3$  will be used to denote both triazole and imidazole ring systems.

#### Synthesis

10

The compounds of this invention can be prepared from chloromethylsilanes and 1,2,4-triazole or imidazole sodium salt or their methylated homologs:

Lithium and potassium azole salts may also be used. Bromomethylsilanes, iodomethylsilanes, or arylsulfonyloxymethylsilanes may be used instead of chloromethylsilanes. Roughly equimolar amounts of the reagents are used (except when  $R_3 = OR_6$ ; see below), with the azole salt often taken in 5-10% excess of theory. In addition, 1,2,4-triazole or imidazole themselves can be used if an acid acceptor is added. Suitable accep-20 tors include excess azole, alkali metal alkoxides such as sodium methoxide or potassium tert-butoxide, inorganic bases such as potassium carbonate, or sodium hydride, and tertiary amines such as triethylamine. When the acid acceptor is a good nucleophile, such as 25 sodium methoxide, an excess should be avoided to prevent undesired side reactions. Suitable solvents include polar aprotic solvents such as dimethylformamide, dimethyl sulfoxide, or acetonitrile; ethers such as tetrahydrofuran or 1,2-dimethoxyethane; and 30 ketones such as 2-butanone. The reaction temperature can vary between 0° and 200°C, preferably between 25° and 100°C. The reaction can be conducted under elevated pressure, but it is generally preferable to operate at atmospheric pressure. The optimum temperature and reaction time will vary with the concentration and choice of reagents, and especially with the choice of solvent. For example, 1,2,4-triazole and sodium methoxide at roughly 2 molar concentration in dimethylformamide gives good conversion in approximately 2 hours at 80-90°C, whereas 1,2,4-triazole and potassium carbonate at roughly 1 molar concentration in 2-butanone requires 8-12 hours at reflux. The imidazole reactions are generally more rapid. In general, reaction times of 1 to 24 hours are required.

Progress of the reaction can be followed by working up aliquots for nmr analysis and following the intensities of the starting material SiCH<sub>2</sub>Cl singlet near 2.9 and the product SiCH<sub>2</sub>N singlets, which are near 3.8 for compounds of Formula I and near 3.7 for compounds of Formula II.

With respect to the triazole derivatives of Formula I, the lH-1,2,4-triazol-1-ylmethyl compound as prepared above is accompanied by a minor amount of the isomeric 4H-1,2,4-triazol-4-ylmethyl compound:

The ratio of isomers varies with values of R and reaction conditions, with a 1-substituted to 4-substituted ratio of roughly 10:1 often observed. The mono- and dimethyltriazoles give similar 4H-isomers as minor products:

When the unsubstituted silylmethyltriazole is available, metalation-methylation provides an alternate synthesis of the methylated homologs:

with respect to the imidazole derivatives of Formula II, isomers are possible only when  $\mathbb{Q}_2$  and 10  $\mathbb{Q}_2$  are not the same. Two isomers result:

The product of Formula IIA will generally predominate. If desired, the isomers may be separated by standard techniques such as crystallization, distillation, or chromatography.

For the case where R<sub>3</sub> = OR<sub>6</sub> in the triazole or imidazole product, the chlorines of a chloro(chloromethyl)silane can be replaced in one of two ways. In one method, at least two equivalents of the azole sodium salt can be used. An intermediate containing a very reactive silicon-azole bond forms, and reaction with water or an alcohol gives the desired oxygenated compounds:

10 
$$R_1$$
- $\sin$ - $\cot$ 2  $\cot$ 2  $\cot$ 4  $\cot$ 4  $\cot$ 5  $\cot$ 6  $\cot$ 6  $\cot$ 7  $\cot$ 8  $\cot$ 9  $\cot$ 9  $\cot$ 9  $\cot$ 10  $\cot$ 1

Suitable solvents and reaction conditions are the same as those outlined on pages 11, 12 and 13 for azole displacements. The temperature of alcoholysis is not critical, and warming to  $50-100^{\circ}\text{C}$  can be used to ensure complete reaction when  $R_6 = C_1 - C_4$  alkyl. For  $R_6 = H$ , however, hydrolysis is best conducted near room temperature to minimize disiloxane formation, recognizing that silanol-disiloxane equilibrium is possible whenever  $R_6 = H$ :

30 
$$_{2}$$
  $_{1}^{R_{2}}$   $_{0}^{R_{1}}$   $_{0}^{R_{1}}$   $_{0}^{R_{2}}$   $_{0}^{R_{$ 

The position of equilibrium and the rate at which it is established will vary with the values of  $R_1$  and  $R_2$ , solvent, temperature, and the presence or absence of acidic or basic catalysts.

In the second method, the silicon-oxygen bond is formed first, followed by azole displacement as described earlier:

$$\xrightarrow{R_1-S_1-CH_2N} \xrightarrow{R_2} \xrightarrow{N} \xrightarrow{N} \xrightarrow{Q_1} \xrightarrow{N} \xrightarrow{Q_2}$$

Reaction of the chlorosilane with R<sub>6</sub>OH may be conducted in almost any non-hydroxylic solvent, with ethers such as diethyl ether, 1,2-dimethoxyethane, and tetrahydrofuran or dipolar aprotic solvents such as dimethylformamide and acetonitrile being preferred. Although an acid acceptor is not required, it is preferred to add a tertiary amine such as triethylamine or pyridine. The reaction temperature may vary from 0° to 100°C, and R<sub>6</sub>OH is often taken in excess of theory. The combination of 2 equivalents of R<sub>6</sub>OH, 1.1 equivalents of triethylamine, and 0.1 equivalents of imidazole in dimethylformamide at 80° for two hours has been broadly applicable.

Extending these methods to (chloromethyl)dichlorosilanes provides dioxygenated silanes:

Glycol derivatives are formed similarly, using a diol instead of two molecules of  $R_6^{\rm OH}$ .

An alternative synthesis for alkoxy(chloromethyl)silanes involves selective replacement of one 5 alkoxy group of a dialkoxysilane with an organometallic reagent:

$$\begin{array}{c} (R_60)_2 \stackrel{R_2}{\text{Si-CH}}_2 \text{Cl} & \xrightarrow{R_1 \text{MgX},} & R_1 \stackrel{R_2}{\text{OR}}_6 \\ & & \text{or } R_1 \text{Na} \end{array}$$

10

30

Conditions for this displacement are as described in the next paragraph, with the added stipulation that the organometallic should be added to the dialkoxy-15 silane.

The required chloromethylsilane starting materials are made from commercially available chloro-(chloromethyl)dimethylsilane, chloromethyl(dichloro)methylsilane, or chloromethyltrichlorosilane:

The Si-Cl bonds in these compounds react with organolithium, organosodium, or Grignard reagents to introduce alkyl and/or aryl groups according to literature procedures, leaving the C-Cl bond intact. For the silanes containing two or three Si-Cl bonds, stepwise replacements are possible, giving considerable flexibility to the values of  $R_1-R_3$ . Bromosilanes, iodosilanes, or alkoxysilanes may be substituted for chlorosilanes in these reactions. Preferred solvents

for these reactions include ethers such as tetrahydro-35

furan, 1,2-dimethoxyethane, and diethyl ether, or hydrocarbons such as hexane and toluene. The preferred temperature will vary between -80° and 40° depending on the nature of the organometallic reagent, 5 how it was generated, and the solvent. For example, when aryllithium reagents are generated in tetrahydrofuran from aryl bromides using butyllithium, the mixture should be held below roughly -40° to avoid side reactions involving the bromobutane produced. 10 organometallic solution is stable at higher temperatures, however, reactions may be run at -20° to 25° without competing reaction of the CH2Cl group. reaction is rapid at all temperatures, and only a short period, for example 30 to 60 minutes, is re-15 quired after the reagents are combined to ensure complete reaction.

Reactions of ClSi(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Cl with Grignard reagents are described by C. Eaborn and J. C. Jeffrey, J. Chem. Soc., 1954, 4266; and a recent review on synthesis of aryltrimethylsilanes from ClSi(CH<sub>3</sub>)<sub>3</sub>, which contains experimental procedures useful for ClSi(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Cl reactions, is that of D. Habich and F. Effenberger, Synthesis, 1979, 841. Selective introduction of one new alkyl group into Cl<sub>2</sub>Si(CH<sub>3</sub>)CH<sub>2</sub>Cl is described by V. P. Kuznetsova and R. M. Sokolovaskaya, Zh. Obshch. Khim., 1969, 1977; Chem. Abstr., 72, 31897 p; and one aryl group may be introduced selectively as well:

In both cases the organometallic reagent should be added to the dichlorosilane at low temperature with good mixing for best yields.

Reactions of Cl<sub>3</sub>SiCH<sub>2</sub>Cl with Grignard reagents are described by A. A. Zhdanov, V. I. Pakhomov, and T. Bazhanova, <u>Zh. Obshch. Khim.</u>, <u>1973</u>, 1280; <u>Chem. Abstr.</u>, <u>79</u>, 66452 m. Adding organometallic reagents to the trichlorosilane is recommended even when three identical groups are being introduced, because adding Cl<sub>3</sub>SiCH<sub>2</sub>Cl to an organometallic reagent is not usually successful. A single aryl group may also be introduced:

A useful modification of literature procedures, applicable when R<sub>1</sub> or R'<sub>1</sub> is an aryl group, has been developed in the present work. Instead of preforming an organolithium reagent and then combining it with a chlorosilane, it has been found that an aryl bromide and a chlorosilane such as ClSi(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Cl may be combined in an inert solvent such as tetrahydrofuran and treated at -80 to -40° with butyllithium. Bromine-lithium exchange proceeds selectively, and the resulting aryllithium reacts with the Si-Cl bond as it is formed:

This reaction works equally well for aryl-substituted chlorosilanes such as  $ClSi(CH_3)(C_6H_5)CH_2Cl$ , and it can be used to introduce two aryl groups into  $Cl_2Si(CH_3)CH_2Cl$ . In a further extension, an aryl and an n-butyl group may be introduced in one step:

Substitution of other alkyllithiums RLi for n-butyllithium provides a general route to Ar(CH<sub>3</sub>)Si(R)CH<sub>2</sub>Cl.

In the following examples, temperatures are reported in degrees Celsius. Abbreviations for nuclear magnetic resonance (nmr) spectra are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; peak positions are reported as parts per million downfield from internal tetramethylsilane. Infrared (ir) peak positions are given in reciprocal centimeters (cm<sup>-1</sup>). Hexanes refers to the mixture of isomers boiling 68-69°, and ether refers to diethyl ether.

25

20

#### Example 1

Preparation of (1,1'-8iphenyl-4-yl)(chloromethyl)dimethylsilane

A solution of 9.9 g (0.042 mol) of 4-bromobi-5 phenyl in 50 ml of dry tetrahydrofuran was cooled to -78° under nitrogen and stirred while 26.5 ml (0.042 mol) of 1.6 molar n-butyllithium in hexane was added dropwise over 15 minutes. A thick slurry formed, and 35 ml of tetrahydrofuran was added to facilitate stirring. With continued cooling, 5.9 ml (6.7 g, 0.046 mol) of chloro(chloromethy)l)dimethylsilane was added over 10 minutes, giving a clear solution that was allowed to warm to room temperature. Addition of 300 ml of ether, filtration to remove precipitated lithium 15 chloride, and evaporation of the filtrate left 13.2 g of semisolid. Redissolution in ether, filtration, and evaporation of the filtrate left 11.0 g (100% crude) of the title compound as a colorless solid, m.p. 30-40°, suitable for further reaction. Trace impuri-20 ties could be removed by sublimation at 30°/0.1 mm, leaving the title compound unsublimed in 83% recovery: m.p. 37-40°; ir (Nujol<sup>R</sup>) 1585, 1240, 1110, 830, 810, 750, 690 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.4 (6H, s), 2.9 (2H, s), 7.3-7.7 (9H, m).

25

Preparation of (4-Bromophenyl)(chloromethyl)dimethyl-silane

4-Bromophenylmagnesium bromide was prepared from 5 11.8 g (0.050 mol) of 1,4-dibromobenzene and 1.2 g (0.050 g-atom) of magnesium turnings in 75 ml of ether according to G. P. Schiemenz, Org. Syn., Coll. Vol. 5, 496 (1973). The resulting mixture was chilled in ice under a nitrogen atmosphere while a solution of 6.6 ml 10 (7.2 g, 0.050 mol) of chloro(chloromethyl)dimethylsilane in 10 ml of ether was added dropwise. The reaction mixture was then stirred overnight at room temperature, quenched carefully with saturated aqueous ammonium chloride, and filtered. The ether phase of 15 the filtrate was washed with brine, dried over magnesium sulfate, and evaporated to leave 9.8 g of an oil. Distillation gave 3.8 g (29%) of the title compound as a colorless liquid: bp 97° (1 mm); ir (neat) 2950, 1575, 1475, 1370, 1250, 1065, 1010, 840, 20 805, 720 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.4 (6H, s), 2.9 (2H, s), 7.3-7.7 (4H, m).

25

.

Preparation of Chloromethyl(4-chlorophenyl)dimethyl-silane

A solution of 9.6 g (0.050 mol) of 4-bromo
chlorobenzene and 6.6 ml (7.2 g, 0.050 mol) of chloro(chloromethyl)dimethylsilane in 75 ml of tetrahydrofuran was stirred at -78° under nitrogen while 31 ml
(0.050 mol) of 1.6 molar n-butyllithium in hexane was
added dropwise. The resulting clear solution was

allowed to warm to room temperature, diluted with
ether until no more lithium chloride precipitated, and
filtered. Evaporation of the filtrate left 10.6 g of
a light yellow liquid, which was distilled to give 6.0
g (55%) of the title compound as a colorless liquid:

bp 54-58°C (0.05 mm); ir (neat) 2910, 1560, 1470,
1370, 1250, 1080, 1010, 840, 805, 790, 740 cm<sup>-1</sup>; nmr
(CDCl<sub>3</sub>) 0.4 (6H, s), 2.9 (2H, s), 7.1-7.6 (4H, q).

The <u>in situ</u> aryllithium generation described in this example is also useful for preparing the product of Example 1. If the reaction is run at 0.5-0.7 molar in 4-bromobiphenyl and the temperature is held at -65 to -55°C during butyllithium addition, little or no solid precipitates.

25

Preparation of Chloromethyl(2,4-dichlorophenyl)-dimethylsilane

A solution of 17.0 g (0.075 mol) of 2,4-dichlorobromobenzene and 10.8 ml (11.8 g, 0.082 mol) of
chloro(chloromethyl)dimethylsilane in 100 ml of dry
tetrahydrofuran was chilled to -70° under nitrogen
and stirred while 49 ml (0.079 mol) of 1.6 molar
n-butyllithium in hexane was added dropwise at a rate
that held the mixture below -70°. The resulting
cloudy reaction mixture was allowed to warm to room
temperature, poured into 400 ml of hexanes, filtered,
and evaporated to leave 20.5 of yellow liquid. Distillation gave 12.6 g (66%) of the title compound as
a colorless liquid: bp 83° (0.02 mm); n<sup>24</sup> 1.5522;
ir (neat) 1565, 1455, 1360, 1255, 1120, 1100, 1040,
825 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.5 (6H, s), 3.1 (2H, s),
7.0-7.5 (3H, m).

Preparation of Chloromethyl(2,6-dimethoxyphenyl)-dimethylsilane

A solution of 25.0 g (0.181 mol) of 1,3-dime-5 thoxybenzene in 250 ml of tetrahydrofuran was stirred at room temperature under nitrogen while 125 ml (0.200 mol) of 1.6 molar  $\underline{n}$ -butyllithium in hexane was added dropwise over 30 minutes. The resulting mixture was refluxed 1.5 hour, giving an orange-brown solution 10 that was cooled to 5° and stirred while 27 ml (29.4 g, 0.205 mol) of chloro(chloromethyl)dimethylsilane was added dropwise over 15 minutes. The resulting white suspension was allowed to warm to room temperature, stirred there 1 hour, diluted with ethyl acetate, poured into water, and extracted with ether. organic layers were washed with brine, dried over magnesium sulfate, and distilled to give 37.0 g (84%) of the title compound as a colorless liquid: bp 98-110° (0.1 mm); nmr (CDCl<sub>3</sub>) 0.4 (6H, s), 3.1 (2H, s), 3.7 (6H, s), 6.3 (2H, d), 7.1 (1H, m).

By varying the organolithium or Grignard reagent, the procedures of Examples 1-5 can be used to prepare the compounds of Table I. Closely related procedures are also known in the literature, for example the use of arylmagnesium chlorides by C. Eaborn and J. C. Jeffrey, J. Chem. Soc., 1954, 4266. For compounds where R<sub>1</sub> is a phenyl ring bearing a 2-halo substituent, an alternative to the <u>in situ</u> procedure of Example 4 is the special arylmagnesium iodide method of C. Eaborn, K. L. Jaura, and D. R. M. Walton, J. Chem. Soc., 1964, 1198.

#### Table I

CH<sub>3</sub> X-Si-CH<sub>2</sub>Cl CH<sub>3</sub>

5

```
bp 127-128°
                                       bp 172°
   n-C4H9
10
                                        n_D^{23} 1.4510
    n-C12H25
                                        n<sub>D</sub><sup>22</sup> 1.4556
    n-C18H37
    cyclopropyl
    cyclopentyl
                                        bp 120-130° (10 mm)
15 cyclohexyl
                                        bp 112° (0.08 mm)
    1-naphthy1
    2-naphthy1
                                        bp 85-86° (3 mm)
    phenyl
                                        bp 59-60° (0.1 mm)
    4-fluorophenyl
                                        bp 80° (0.05 mm)
20 4-methoxyphenyl
                                        bp 122° (0.03 mm)
    4-phenoxyphenyl
                                        n_D^{22} 1.5773
    4-(4-chlorophenoxy)phenyl
    4-(4-fluorophenoxy)phenyl
    4-(4-trifluoromethylphenoxy)phenyl
    4-(4-methylphenoxy)phenyl
                                        bp 92-93° (0.05 mm)
     4-thiomethylphenyl
                                        n<sub>D</sub><sup>23</sup> 1.4686
     4-trifluoromethylphenyl
                                        bp 96° (7 mm)
     4-methylphenyl
     4-i-propylphenyl
                                        n_{\rm D}^{23} 1.5056
30
     4-t-butylphenyl
                                        m.p. 64-68°
     4-methylsulfonylphenyl
                                        n_D^{21} 1.5424
     4-cyclohexylphenyl
                                        bp 55-57° (0.15 mm)
     4-trifluoromethoxyphenyl
     4-(4-chlorophenyl)phenyl
```

4-(4-bromophenyl)phenyl

# Table I (continued)

# $X = R_1 \text{ or } R_1^*$

5	4-(4-methylphenyl)phenyl	
	4-(4-trifluoromethylphenyl)phenyl	
	4-(4-fluorophenyl)phenyl	
	3-phenylphenyl	n <mark>20</mark> 1.5862
	3-trifluoromethylphenyl	bp 59-62° (0.3 mm)
10	3-chlorophenyl	bp 73° (0.15 mm)
	2-trifluoromethylphenyl	n <sub>D</sub> <sup>23</sup> 1.4826
	2-phenylphenyl	n <sup>20</sup> 1.5772
	2-chlorophenyl	bp 78-80° (0.3 mm)
	2-methoxyphenyl	n <sub>D</sub> <sup>21</sup> 1.5164
15	2,3-dimethylphenyl	
	2,3-dimethoxyphenyl .	n <sub>D</sub> <sup>22</sup> 1.5254
	2,4-difluorophenyl	•
	2-fluoro-4-chlorophenyl	
	2-chloro-4-phenylphenyl	
20	2-fluoro-4-phenylphenyl	
	2-methyl-5-chlorophenyl	
	2,6-dimethylphenyl	
	3,4-dichlorophenyl	bp 98° (0.6 mm)
	3-methyl-4-fluorophenyl	
25	3,5-dichlorophenyl	bp 94-95° (0.25 mm)

Preparation of (1,1'-Biphenyl-4-yl)butyl(chloromethyl)methylsilane

The title compound can be prepared by the proce5 dure of Example 1 by substituting (butyl)chloro(chloromethyl)methylsilane for chloro(chloromethyl)dimethylsilane.

Related compounds can be prepared by the procedures of Examples 1-5, using the appropriate organolithium or Grignard reagent and Cl(R<sub>2</sub>)Si(CH<sub>3</sub>)CH<sub>2</sub>Cl. The required chloromethylsilane starting materials are made from R<sub>2</sub>MgCl or R<sub>2</sub>Li and Cl<sub>2</sub>Si(CH<sub>3</sub>)CH<sub>2</sub>Cl according to Examples 14 and 15, and literature procedures such as V. P. Kuznetsova and R. M. Sokolovaskaya, Zh.

15 Obshch. Khim., 1969, 1997.

Alternatively, both the biphenyl and butyl groups can be introduced simultaneously as follows: A solution of 23.3 g (0.10 mol) of 4-bromobiphenyl and 12.7 ml (16.4 g, 0.10 mol) of chloromethyl(dichloro)methylsilane in 150 ml of dry tetrahydrofuran was chilled under nitrogen to -70° and stirred while 125 ml (0.20 mol) of 1.6 molar  $\underline{n}$ -butyllithium in hexane was added at a rate that held the mixture below -60°C. The resulting thin slurry was allowed to warm to room 25 temperature, treated cautiously with 10 ml of ethyl acetate, and poured into 300 ml of water. The organic layer was separated, the aqueous phase was washed with another 100 ml of hexanes, and the combined organic phases were washed three times with water, once with 30 brine, dried over magnesium sulfate, and evaporated to leave 33.9 g of a viscous yellow oil. Distillation gave 9.5 g (31%) of the title compound: bp 135-158°  $(0.1 \text{ mm}); n_{D}^{22} 1.5743; \text{ ir (neat) } 3060, 3015, 2960,$ 2920, 2870, 1600, 1485, 1390, 1380, 1250, 1120, 1075, 35 1005, 875, 810, 800, 760, 700 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>): 0.4 (3H, s), 0.6-1.8 (9H, m), 2.9 (2H, s) and 7.0-7.7 (9H, m).

Preparation of Butyl(chloromethyl)(4-chlorophenyl)methylsilane

A solution of 14.4 g (0.075 mol) of 4-bromo-5 chlorobenzene and 9.5 ml (12.3 g, 0.075 mol) of chloromethyl(dichloro)methylsilane in 150 ml of tetrahydrofuran was cooled to -60° under nitrogen and stirred while 94 ml (0.15 mol) of 1.6 molar  $\underline{n}$ -butyllithium in hexane was added dropwise at a rate that held 10 the mixture between -65 and -55°. The resulting slurry was allowed to warm to room temperature, giving a solution that was diluted with hexanes until no more lithium chloride precipitated. Filtration, evaporation of the filtrate, dissolution of the residue in 15 hexanes, refiltration, and evaporation left 19.8 g of a pale orange liquid. Distillation gave first 1.8 g (12%) of chloromethyl(dibutyl)methylsilane, bp 45°C (0.05 mm), followed by  $6.8~\mathrm{g}$  (35%) of the title compound as a colorless liquid: bp 90°C (0.05 mm);  $n_{\rm D}^{21}$  1.5246; ir (neat) 2925, 1580, 1380, 1260, 1090, 1015, 820, 740 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.4 (3H, s), 0.6-1.5 (9H, m), 2.9 (2H, s), 7.0-7.4 (4H, q).

25

Preparation of Chloromethyl(2,4-dichlorophenyl)methyl-(phenyl)silane

A solution of 13.6 g (0.060 mol) of 2,4-dichloro-5 bromobenzene and 12.3 g (0.060 mol) of chloro(chloromethyl)methyl(phenyl)silane (prepared as in Example 14) in 85 ml of dry tetrahydrofuran was chilled to -60° under nitrogen and stirred while 38 ml (0.060 mol) of 1.6 molar  $\underline{n}$ -butyllithium in hexane was added 10 dropwise at a rate that held the mixture below -55°. The resulting red solution was allowed to warm to room temperature, treated with 5 ml of ethyl acetate to quench any unreacted organolithium reagent, and poured into 170 ml of water. The organic layer was sepa-15 rated, the aqueous phase was washed with 50 ml of hexanes, and the combined organic phases were washed three times with water and once with brine, dried over magnesium sulfate, and evaporated to leave 19.0 g of bright yellow oil. Distillation gave 8.6 g (45%) of 20 the title compound as a colorless liquid: b.p. 125-130° (0.05 mm);  $n_D^{21}$  1.5978; ir (neat) 3080, 3060, 2960, 2930, 1570, 1540, 1460, 1430, 1365, 1260, 1120, 1100, 1040, 820, 745, 735, 705 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.8 (3H, s), 3.4 (2H, s), 7.2-7.9 (8H, m).

25

Preparation of Chloromethyl[bis(4-chlorophenyl)]methylsilane

A solution of 19.1 g (0.10 mol) of 4-chloro-5 bromobenzene in 200 ml of dry tetrahydrofuran was chilled to -60° under nitrogen and stirred while 63 ml (0.10 mol) of 1.6 molar n-butyllithium in hexane was added dropwise at a rate that held the mixture below -55°. Stirring and cooling were continued while 6.3 10 ml (8.2 g, 0.05 mol) of chloromethyl(dichloro)methylsilane was added dropwise at a rate that held the mixture below -50°. The resulting orange solution was allowed to warm to room temperature, and workup as in Example 8 provided 16.5 g of a pale yellow oil. 15 Kugelrohr distillation at 0.05 mm and an airbath temperature of 130-150°C gave 9.5 g (60%) of the title compound as a colorless liquid:  $n_n^{24}$  1.5913; ir (neat) 3080, 3040, 3020, 2960, 2930, 1580, 1490, 1380, 1260, 1085, 1015, 805, 790, 775, 740 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.7 (3H, s), 3.1 (2H, s), 7.2-7.7 (8H, m);

analysis for  $C_{14}H_{13}Cl_3Si$  (mw 315.70):

Calculated: C, 53.26; H, 4.15; Cl, 33.69. Found: C, 53.4; H, 4.4; C1, 34.2. 53.5; 4.4; 34.1.

25

Preparation of (Chloromethyl)bis(4-fluorophenyl)methylsilane

A solution of 35 g (0.20 mol) of 4-fluorobromobenzene in 300 ml of dry tetrahydrofuran was chilled
to -60° under nitrogen and stirred while 126 ml (0.20
mol) of 1.6 molar n-butyllithium in hexane was added
dropwise at a rate that held the mixture below +55°.
Stirring and cooling were continued while 12.6 ml

10 (16.4 g, 0.10 mol) of chloromethyl(dichloro)methylsilane was added dropwise at a rate that held the mixture below -50°. The resulting solution was allowed
to warm to room temperature, and workup as in Example
8 provided 26.4 g of a clear yellow liquid. Distil15 lation gave 20.6 g (73%) of the title compound as a
colorless liquid: bp 107-127° (0.1 mm); n<sub>D</sub><sup>22</sup> 1.5481;
nmr (CDCl<sub>3</sub>): 0.7 (3H, s), 3.2 (2H, s), 7.1 (4H, t,
J = 9) and 7.6 (4H, d of d, J = 6 and 9).

Repeating this reaction using chloromethyl(diethoxy)methylsilane instead of the dichlorosilane gave the title compound in 58% yield after distillation: bp 115-138° (0.2 mm);  $n_D^{21}$  1.5464; nmr as above.

## Example 11

25 Preparation of Chloromethyl(2-chlorophenyl)(4-chlorophenyl)methylsilane

A solution of 6.3 ml (8.2 g, 0.05 mol) of chloromethyl(dichloro)methylsilane and 8.1 g (0.05 mol) of 2-bromochlorobenzene in 75 ml of dry tetrahydrofuran was chilled to -60° under  $N_2$  and stirred while 31 ml (0.05 mol) of 1.6 molar n-butyllithium-hexane solution was added at a rate that held the mixture below -55°. With continued cooling and stirring, 8.1 g (0.05 mol) of 4-bromochlorobenzene was added as a solid, followed by another 31 ml portion of the 1.6

molar n-butyllithium solution at a rate that held the mixture below -55°C. The resulting thin slurry was allowed to warm to room temperature, treated cautiously with 10 ml of ethyl acetate, and worked up as in Example 8 to give 15.0 g of a clear yellow oil. Oistillation provided 5.9 g (37%) of the title compound: bp 150-165° (0.7 mm); n<sub>D</sub><sup>20</sup> 1.5916; ir (neat) 3060, 3020, 2960, 2920, 2870, 1580, 1560, 1490, 1420, 1380, 1255, 1125, 1115, 1085, 1035, 1015, 805, 750 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.8 (3H, s), 3.3 (2H, s), 7.2-7.7 (8H, m).

The compounds of Fable II are made by stepwise replacement of the Si-Cl bonds of  $\rm Cl_2Si(CH_3)CH_2Cl$ , according to the procedures of Examples 6-11.

#### Table II

x-si-ch<sub>2</sub>c:

5

C,H5 10 cyclohexyl bp 45° (0.05 mm) U-CVH2 cyclopropyl 3-methylbutyl n-C<sub>18</sub>H<sub>37</sub> n-C6H13 cyclopropyl 15 cyclohéxyl cyclohexyl 1-naphthy1 t-CAHo <u>n</u>-C<sub>5</sub>H<sub>11</sub> 2-naphthy1 n-C-H-7 phenyl bp 82-90°(0.1 mm) 20 phenyl n-CAHo 1,1-dimethylpropyl pheny1 4-phenylphenyl C2H5 1-C3H7 4-bromophenyl bp 90-92°(0.1 mm) 4-fluorophenyl n-C4H9 25 4-phenoxyphenyl t-CAH9 cyclopenty1 4-t-butylphenyl S-CAH9 3-trifluoromethylphenyl n-C5H11 3-chlorophenyl 2-thiomethylphenyl cyclobutyl i-CAH9 30 2-phenylphenyl bp 109-112°(0.1 mm) r-CAH9 2,4-dichlorophenyl cyclopropyl 2,4-dichlorophenyl n-C3H7 2,3-dimethylphenyl cyclopentyl 2-methyl-5-fluorophenyl 4-methylpentyl 35 2,5-dimethoxyphenyl

	$X = R_1, R_1'$	R <sub>2</sub>	
	2,6-dimethylphenyl	l-methylbutyl	
5	3,5-dichlorophenyl	n-C4H9	
	3,5-dichlorophenyl	cyclohexyl	
	3-methyl-4-chlorophenyl	cyclopropyl	
	phenyl	prioriy =	bp 104-110°(0.2 mm)
	4-fluorophenyl	p , _	n <sub>D</sub> <sup>22</sup> 1.5624
10	4-chlorophenyl	Pr7 —	bp 140-148°(0.1 mm)
	4-bromophenyl	phenyl	bp 145-155°(0.1 mm)
	4-phenylphenyl	phenyl	bp 173-178°(0.1 mm)
	4-t-butylphenyl	phenyl ·	
	4-thiomethylphenyl	phenyl	
15	4-phenoxyphenyl	phenyl	
	4-trifluoromethoxyphenyl	phenyl	
	4-methylsulfonylphenyl	phenyl	
	4-cyclohexylphenyl	phenyl	
	4-(4-fluorophenyl)phenyl	phenyl	
20	3—trifluoromethylphenyl	phenyl	
	2-chlorophenyl	phenyl	bp 132-135°(0.1 mm)
	2-methoxyphenyl	phenyl	
	2-chloro-4-phenylphenyl	phenyl	
	2-fluoro-4-phenylphenyl	phenyl	•
25	3,5-dichlorophenyl	phenyl	•
	2,5-dimethoxyphenyl	phenyl	•
	2,6-dimethoxyphenyl	phenyl	bp 160-170°(0.1 mm)
	4-bromophenyl .	4-bromophenyl	m.p. 115-117°
	4-phenylphenyl	4-phenylphenyl	bp 166-171°(0.1 mm)
30	4-methoxyphenyl	4-methoxyphenyl	•
	3-trifluoromethylphenyl	3-trifluoromethylp	reigt
	2-methoxyphenyl	2-methoxyphenyl	bp 135-140°(0.1 mm)
	2-chlorophenyl	2-chlorophenyl	
	2,4-dichlorophenyl	2,4-dichloropheny	<del>-</del>
35	3,5-dichlorophenyl	3,5-dichloropheny	T

35
Table II (continued)

	$X = R_1, R_1'$	<u>R2</u>
	2-chlorophenyl	4-fluorophenyl
5	4-phenylphenyl	4-chlorophenyl
	4-phenylphenyl	4-fluorophenyl
	4-phenylphenyl	2,4-dichlorophenyl
	4-fluorophenyl	2,4-dichlorophenyl
	4-chlorophenyl	2,4-dichlorophenyl
10	1-naphthy1	2,6-dimethoxypheny
	/_nhenoxynheny1	3.4-dichlorophenyl

25 .

Preparation of (1-1'-Biphenyl-1-yl)(chloromethyl)-diethylsilane

The title compound can be prepared by the proce-5 dure of Example 1, using chlorochloromethyldiethylsilane instead of chlorochloromethyldimethylsilane.

Similar compounds can be prepared by applying the procedures of Examples 1-5 to the appropriate organolithium or Grignard reagent and  $Cl(R_2)Si(R_3)CH_2Cl$ .

The required chlorochloromethyldialkylsilanes are made from  $Cl_3SiCH_2Cl$ , using two equivalents of  $R_2MgCl$  or  $R_2Li$  when  $R_2=R_3$  (see, for example, A. A. Zhdanov,

V. I. Pakhomov, and T. Bazhanova, <u>Zh. Obshch. Khim.</u>, 1973, 1280), or using one equivalent of R<sub>2</sub>MgCl or

15  $R_2Li$  followed by one equivalent of  $R_3MgCl$  or  $R_3Li$  when  $R_2$  is not equal to  $R_3$ .

20

25

30

# Preparation of (Chloromethyl)triphenylsilane

A solution of 12.6 ml (18.4 g, 0.10 mol) of (chloromethyl)trichlorosilane in 150 ml of dry ether

5 was stirred under nitrogen and chilled in ice while 162 ml (0.30 mol) of 1.85 molar phenyllithium in cyclohexane-ether 70:30 was added dropwise at a rate that held the mixture below 15°C. The resulting slurry was stirred overnight at room temperature, treated carefully with 10 ml of ethyl acetate to quench any remaining phenyllithium, washed with water and brine, dried over magnesium sulfate, and evaporated to leave 33 g of sticky solid. Recrystallization from 30 ml of cyclohexane provided 15.8 g (51%) of the title compound as an off white solid: m.p. 112-115°C; ir (Nujol<sup>R</sup>) 1420, 1110, 735, 730, 705, 695 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 3.5 (2H, s), 7.0-7.8 (15H, m).

The compounds of Table III are made by stepwise replacement of the Si-Cl bonds of Cl<sub>3</sub>SiCH<sub>2</sub>Cl, according to the procedures of Examples 12-13.

25

20

# Table III

R<sub>2</sub> X-Si-CH<sub>2</sub>Cl

	Y - P P!	R.	R_
	$\frac{X = R_1, R_1'}{R_1'}$	<u>-2</u>	<u>3</u>
	<sup>С</sup> 2 <sup>Н</sup> 5	C2H5	C <sub>2</sub> H <sub>5</sub>
10	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	i-C3H7	<u>i</u> -C <sub>3</sub> H <sub>7</sub>
	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>n</u> -C4H9	n-C4H9
	<u>n</u> -C <sub>8</sub> H <sub>17</sub>	<sup>C</sup> 2 <sup>H</sup> 5	cyclopentyl
	<u>n</u> -C <sub>14</sub> H <sub>29</sub>	cyclopropyl	1-methylbutyl
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	<u>n</u> -c <sub>6</sub> H <sub>13</sub>	<u>n</u> -C <sub>6</sub> H <sub>13</sub>
15	cyclopropyl	С <sub>2</sub> Н <sub>5</sub>	<u>s</u> -C <sub>4</sub> H <sub>9</sub>
	cyclohexyl	<u>n</u> -C <sub>3</sub> H <sub>7</sub>	<u>n</u> -c <sub>3</sub> H <sub>7</sub>
	l-naphthyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
	2-naphthyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	cyclobutyl
	phenyl	cyclopropyl	<u>u</u> -c <sup>4</sup> 13
20	4-phenylphenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
	4-phenylphenyl	n-C6H13	<u>n</u> -C <sub>6</sub> H <sub>13</sub>
	4-phenylphenyl	cyclohexyl	cyclohexyl
	4-chlorophenyl	n-C4H9	n-C4H9
	4—fluorophenyl	n-C <sub>3</sub> H <sub>7</sub>	<u>n</u> -C <sub>3</sub> H <sub>7</sub> .
25 <sup>°</sup>	4-phenoxyphenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	cyclohexyl
	4—(4—chlorophenoxy)phenyl	n-C4H9	n-C4H9
	4 <u>t</u> -butylphenyl	s-C4H9	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
	3-methoxyphenyl	C2H5	t-C4H9
	3-trifluoromethylphenyl	S-CAH9	s-C4H9
30	2-thiomethylphenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	3-methylbutyl
	2-phenylphenyl	cyclohexyl	cyclohexyl
	2,4-dichlorophenyl	n-CAH9	<u>n</u> -C4H9
	2,6-dimethylphenyl	t-CAH9	t-CAH9
	3,5-dichlorophenyl	cyclopentyl	cyclopentyl
35	3-methyl-4-chlorophenyl	<u>s</u> -C <sub>4</sub> H <sub>9</sub>	<u>s</u> -C <sub>4</sub> H <sub>9</sub>
			<del></del>

	$X = R_1, R_1'$	R <sub>2</sub>	R <sub>3</sub>
	C <sub>2</sub> H <sub>5</sub>	phenyl	phenyl
5	cyclohexyl	phenyl	phenyl
-	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	phenyl	phenyl
	U-CAH	4-chlorophenyl	4-chlorophenyl .
	<u>n</u> -C <sub>12</sub> H <sub>25</sub>	4-chlorophenyl	4-chlorophenyl
	1-naphthyl	4-fluorophenyl	4-fluorophenyl
10	cyclopropyl	phenyl	4- <u>t</u> -butylphenyl
	n-CaHo	phenyl	4-phenylphenyl
	t-C4H9	phenyl	2,4-dichlorophenyl
	<u>n</u> -C <sub>3</sub> H <sub>7</sub>	phenyl	3-trifluoromethylphenyl
	<u>i</u> -C,H	phenyl	3,5-dichlorophenyl
15	cyclopentyl	phenyl	2,6-dimethoxyphenyl
	n-C14H29	4-chlorophenyl	2-fluorophenyl
	n-C,Ho	4-fluorophenyl	4-phenylphenyl
	4-chlorophenyl	4-chlorophenyl	4-chlorophenyl
	4-fluorophenyl	4-fluorophenyl	4-fluorophenyl
20	4-phenylphenyl	4-phenylphenyl	4-phenylphenyl
	2,4-dichlorophenyl	2,4-dichlorophenyl	2,4-dichlorophenyl
	phenyl	4-fluorophenyl	4-fluorophenyl
	phenyl	4-chlorophenyl	4-chlorophenyl
	phenyl	4-phenylphenyl '	4-phenylphenyl
25	phenyl	2,4-dichlorophenyl	2,4-dichlorophenyl
	2-naphthyl	4-methylthiophenyl	4-methylthiophenyl
	4-chlorophenyl	2-methoxyphenyl	2-methoxyphenyl
	4-chlorophenyl	3-chlorophenyl	3-chlorophenyl
	phenyl	2-chlorophenyl	4-fluorophenyl
30	phenyl	4-chlorophenyl	4-phenylphenyl
	1-naphthyl	4-bromophenyl	3-methylphenyl
	4-phenoxyphenyl	3,5-dimethylphenyl	3,4-dichlorophenyl

# Preparation of Chloro(chloromethyl)methyl(phenyl)silane

A solution of 12.7 ml (16.4 g, 0.10 mol) of chloromethyl(dichloro)methylsilane in 200 ml of ether 5 was chilled to -70° under nitrogen and stirred vigorously while a mixture of 55 ml (0.10 mol) of 1.8 molar phenyllithium in 30:70 ether-cyclohexane and 55 ml of ether was added dropwise at a rate that kept the mixture below -70°. The resulting slurry was stirred and warmed to room temperature, then allowed to stand overnight. Filtration and evaporation of the filtrate left 20.4 g of a golden oil, which was distilled to give 14.6 g (71%) of the title compound as a colorless liquid: bp 71-74° (0.6 mm); n<sub>D</sub><sup>23</sup> 1.5337; ir (neat) 3080, 3060, 2980, 2930, 1590, 1430, 1260, 1120, 820, 790, 740, 700 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.8 (3H, s), 3.1 (2H, s), 7.3-7.6 (3H, m), 7.6-7.8 (2H, m).

#### Example 15

20 Preparation of (1,1'-Biphenyl-4-yl)chloro(chloro-methyl)methylsilane

The title compound can be prepared by reaction of equimolar quantities of 4-bromobiphenyl, chloromethyldichloro(methyl)silane, and n-butyllithium according to the procedure of Example 3.

The compounds of Table IV can be prepared using the procedures of Examples 14 and 15.

#### 41 Table IV

R<sub>2</sub> X-Si-CH<sub>2</sub>C1

```
R 2
                                           СН3
    C2H5
                                           CH<sub>3</sub>
10 t-C4H9
                                           CH<sub>3</sub>
    n-CAH9
                                           C2H5
    n-C12H25
                                           n-C6H13
    n-C<sub>18</sub>H<sub>37</sub>
                                           CH<sub>3</sub>
     cyclopropyl
                                           CH<sub>3</sub>
15 cyclohexyl
                                           1-C3H7
     1-naphthyl
                                           cyclobutyl
     2-naphthyl
                                           t-CAH9
     phenyl
                                           n-C4H9
     4-phenylphenyl
                                           n-C6H13
     4-phenylphenyl
                                           n-CAH9
     4-chlorophenyl
                                           CH<sub>3</sub>
     4-chlorophenyl
                                           n-C6H13
     4-fluorophenyl
                                           cyclohexyl
     4-phenoxyphenyl
                                           n-C3H7
     4-t-butylphenyl
25
                                           CH<sub>3</sub>
     4-trifluoromethoxyphenyl
                                           CH<sub>3</sub>
     4-(4-fluorophenyl)phenyl
                                           t-CAH9
     3-trifluoromethylphenyl
                                            cyclopentyl
     2-thiomethylphenyl
30 2,4-dichlorophenyl
                                            CH<sub>3</sub>
                                            n-C4H9
     2,4-dichlorophenyl
                                            CH<sub>3</sub>
     2-chloro-4-phenylphenyl
                                            cyclopropyl
     2,3-dimethylphenyl
     2-methyl-5-fluorophenyl
                                            s-CAH9
                                            1,1-dimethylpropyl
35 2,6-dimethoxyphenyl
```

	$X = R_1, R_1$	_ <u>R_2</u>
	3-methy1-4-chlorophenyl	с <sub>2</sub> н <sub>5</sub>
5	3,5-dichlorophenyl	<u>n</u> -C <sub>5</sub> H <sub>11</sub>
	<u>n-C<sub>12</sub>H<sub>25</sub></u>	2,4-dichlorophenyl
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	phenyl
	1-naphthy1	phenyl
	pheny1	phenyl
10	4-fluorophenyl	phėnyl
	4-chlorophenyl	phenyl :
	4-phenylphenyl	phenyl
	4- <u>t</u> -butylphenyl	phenyl
	3-fluorophenyl	phenyl
15	2-methoxyphenyl	phenyl
	2-chlorophenyl	phenyl
	2,4-dichlorophenyl	phenyl
	3,5-dichlorophenyl	phenyl
	4-fluorophenyl	4-fluorophenyl
20	4-chlorophenyl	4-chlorophenyl
	4-phenylphenyl	4-phenylphenyl
	2,4-dichlorophenyl	2,4-dichlorophenyl
	3-trifluoromethylphenyl	3-trifluromethylphenyl
	2-methoxyphenyl	2-methoxyphenyl
25	2-chlorophenyl	4-fluorophenyl
	3-trifluoromethylphenyl	4- <u>t</u> -butylphenyl
	2-fluoro-4-chlorophenyl	4-bromophenyl
	2,3-dimethylphenyl	4-methylthiophenyl
	2,6-dimethoxyphenyl	4-methoxyphenyl
30	3,4-dichlorophenyl	4-methylphenyl

Preparation of Chloromethyl(methoxy)methyl(phenyl)silane

A solution of 1.6 ml (1.3 g, 0.040 mol) of
methanol and 3.0 ml (2.2 g, 0.022 mol) of triethylamine in 100 ml of ether was stirred while a solution
of 4.1 g (0.020 mol) of chloro(chloromethyl)methyl(phenyl)silane in 10 ml of ether was added dropwise.
The resulting slurry was refluxed for 2 hours, cooled,
washed with water, 0.1 N aqueous HCl, saturated aqueous NaHCO<sub>3</sub>, water, and brine, dried over magnesium
sulfate, and evaporated to leave 3.2 g of a pale
yellow liquid. Distillation provided 1.7 g (42%) of
the title compound as a colorless liquid: bp 46-49°
(0.05 mm); n<sup>22</sup> 1.5207; nmr (CDCl<sub>3</sub>): 0.5 (3H,
s), 3.0 (2H, s), 3.5 (3H, s) and 7.3-7.8 (5H, m).

#### Example 17

Preparation of Chloromethyl(1,1-dimethylethoxy)methyl-(phenyl)silane

20

A mixture of 15.4 g (0.075 mol) of chloro(chloromethyl)methyl(phenyl)silane, 14 ml (11.1 g, 0.15 mol) of  $\underline{t}$ -butanol, 11.5 ml (8.3 g, 0.082 g) of triethylamine, and 0.5 g (0.008 mol) of imidazole in 60 ml of dimethylformamide was stirred at 80° for 2 hours. resulting slurry was cooled, poured into 200 ml of water, and extracted with ether. The ether extracts were washed three times with water, followed by 0.1  $\underline{N}$ aqueous HCl, saturated aqueous NaHCO3, and brine, dried over magnesium sulfate, and evaporated to leave 14.0 g of a pale orange oil. Distillation provided 11.9 g (65%) of the title compound: bp 78-82° (0.2 mm);  $n_0^{21}$  1.5010; ir (neat) 3080, 3060, 2990, 2940, 1600, 1435, 1395, 1370, 1260, 1245, 1195, 1125, 1060, 35 1030, 815, 790, 740, 725, 705, 650 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>): 0.5 (3H, s), 1.3 (9H, s), 2.9 (2H, s) and 7.3-7.8 (5H, m).

# Preparation of Chloromethyl(ethoxy)methyl(phenyl)silane

A solution of 18.2 ml (18.2 g, 0.10 mol) of chloromethyl(diethoxy)methylsilane in 200 ml of dry

5 ether was stirred vigorously under N<sub>2</sub> and chilled while 56 ml (0.10 mol) of 1.8 molar phenyllithium in 70:30 cyclohexane-ether was added at a rate that held the mixture below -50°. The resulting slurry was allowed to warm to room temperature, treated cautiously with 10 ml of ethyl acetate, washed with water and brine, dried over magnesium sulfate, and evaporated to leave 16.8 g of a golden yellow liquid. Distillation provided 9.5 g (44%) of the title compound as a colorless liquid: bp 80-84° (0.1 mm); n<sub>D</sub> 1.5144;

15 nmr (CDCl<sub>3</sub>) 0.5 (3H, s), 1.2 (3H, t, J = 7), 3.0 (2H, s), 3.8 (2H, q, J = 7), 7.2-7.8 (5H, m).

The compounds of Table V can be prepared using the procedures of Examples 16-18.

20

25

### Table V

R<sub>2</sub> X-Si-CH<sub>2</sub>Cl OR<sub>6</sub>

5

R<sub>2</sub>  $X = R_1, R_1'$ CH<sub>3</sub> CH3 10 CH<sub>3</sub> C2H5 CH<sub>3</sub> C2H5 CH<sub>3</sub> n-C6H13 n-C<sub>18</sub>H<sub>37</sub> S-C4H9 CH<sub>3</sub> cyclopropyl CH<sub>3</sub> CH<sub>3</sub> cyclohexyl 15 1-C3H7 1-C3H7 1-naphthyl D-C3H7 cyclobutyl 2-naphthy1 pheny1 CH<sub>3</sub> bp 72-76°(0.1 mm) CHZ pheny1 t-CAH9 phenyl 20 CH<sub>3</sub> 4-phenylphenyl n-C4H9 Н t-C4H9 4-phenylphenyl C2H5 CH<sub>3</sub> 4-phenylphenyl n-C4H9 CH<sub>3</sub> 4-phenylphenyl n-C4H9 n-C4H9 4-chlorophenyl 25 CH<sub>3</sub> CH<sub>3</sub> 4-chlorophenyl C2H5 CH<sub>3</sub> 4-chlorophenyl n-C3H7 n-C6H13 4-fluorophenyl C2H5 4-fluorophenyl CH<sub>3</sub> cyclohexyl i-CAH9 4-phenoxyphenyl 30 4-t-butylphenyl n-C-H-7 S-CAH9 Н 3-trifluoromethylphenyl t-CAH9  $C_2H_5$ cyclopentyl 2-methylthiophenyl CH<sub>3</sub> 2.4-dichlorophenyl CH3 CH3 C2H5 2,4-dichlorophenyl 35 CHZ t-CAH9 2,4-dichlorophenyl

46
Table V (continued)

	$X = R_1, R_1'$	R <sub>2</sub>	R <sub>6</sub>
	2,4-dichlorophenyl	n-CaH9	C2H5
5	2,3-dimethylphenyl	cyclopropyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>
	2-methyl-5-fluorophenyl	s-CaH9	n-C3H7
	2,6-dimethoxyphenyl	1,1-dimethylpropyl	н
	3-methyl-4-chlorophenyl	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>
	3,5-dichlorophenyl	n-C5H11	C2H5
10	<u>n</u> -C <sub>12</sub> H <sub>25</sub>	2,4-dichlorophenyl	t-C4H9
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	phenyl	CH <sub>3</sub>
	1-naphthyl	phenyl	C2H5
	pheny1	phenyl	t-C4H9
	4-fluorophenyl	pheny1	CH <sub>3</sub>
15	4-chlorophenyl	phenyl	n-C3H7
	4-phenylphenyl	phenyl	C2H5
	4-phenylphenyl	phenyl	<u>s</u> -C <sub>4</sub> H <sub>9</sub>
	4- <u>t</u> -butylphenyl	phenyl	<u>s</u> -C4H9
	3-fluorophenyl	phenyl	C <sub>2</sub> H <sub>5</sub>
20	2-methoxyphenyl	phenyl	Н
	2-chlorophenyl	phenyl	CH <sub>3</sub>
	2,4—dichlorophenyl	phenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>
	3,5-dichlorophenyl	phenyl	n-C3H7
	4-fluorophenyl	4-fluorophenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub>
25	4—fluorophenyl	4-fluorophenyl	<sup>C</sup> 2 <sup>H</sup> 5
	4-chlorophenyl	4-chlorophenyl	CH <sub>3</sub>
	4-chlorophenyl	4-chlorophenyl	<sup>C</sup> 2 <sup>H</sup> 5
	4-phenylphenyl	4-phenylphenyl	CH <sub>3</sub>
70	2,4-dichlorophenyl	2,4-dichlorophenyl	<sup>C</sup> 2 <sup>H</sup> 5
30	3-trifluoromethylphenyl	3-trifluoromethylphenyl	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
	2-methoxyphenyl	2-methoxyphenyl	Н
	2-chlorophenyl	4-fluorophenyl	Н
	3-trifluoromethylphenyl	4- <u>t</u> -butylphenyl	n-C4H9
7 ~	2-fluoro-4-chlorophenyl	4-bromophenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>
35	2,3—dimethylphenyl	4-methylthiophenyl	<sup>C</sup> 2 <sup>H</sup> 5

	$X = R_1, R_1'$	R <sub>2</sub>	<u>R</u> 6
	2,6-dimethoxyphenyl	4-methoxyphenyl	н
5	3,4-dichlorophenyl	4-methylphenyl	<u>i</u> -C4H9

Preparation of (1,1'-8iphenyl-4-yl)dimethyl(1H-1,2,4-triazol-1-vlmethyl)silane

A mixture of 2.6 g (0.010 mol) of (1,1'-biphenyl4-yl)chloromethyldimethylsilane and 1.1 g (0.012 mol)
of 1,2,4-triazole sodium salt in 5 ml of dimethylformamide was warmed to 80-90° for 2 hours, cooled, diluted with water, and extracted with ether. The ether
solution was washed with water and brine, dried over
magnesium sulfate, and evaporated to leave 2.3 g of
colorless solid, m.p. 79-86°. Recrystallization from
a mixture of 25 ml of hexanes and 2 ml of ethyl acetate gave 1.1 g (38%) of the title compound: m.p.
92-93°; ir (Nujol<sup>R</sup>) 1255, 1130, 1000, 825, 760, 695
cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.4 (6H, s), 3.9 (2H, s), 7.2-7.7
(9H, m), 7.8 (1H, s), 7.9 (1H, s); analysis for
C<sub>17</sub>H<sub>19</sub>N<sub>3</sub>Si (mw 293.43):

Calculated C, 69.58; H, 6.53; N, 14.32; Found C, 70.0; H, 6.6; N, 13.9; 69.8; 6.7; 13.8.

An equimolar mixture of 1,2,4-triazole and sodium methoxide can be used instead of preformed triazole sodium salt. Note that these reagents must be combined before the silane is added, since chloromethylsilanes react very vigorously with sodium methoxide in dimethylformamide, giving undesired products.

30

Isolation of (1,1'-Biphenyl-4-yl)dimethyl(4H-1,2,4triazol-4-ylmethyl)silane

A 5 g sample of once-crystallized l,l'-(biphenyl-5 4-yl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane, prepared as in Example I4 using sodium methoxide-1,2,4triazole, was subjected to high pressure liquid chromatography (Waters Prep PAK-500 silica gel cartridge, 250 ml per minute flow rate). Elution with ethyl ace- . 10 tate-hexane 50:50 removed first some minor impurities and then provided the pure 1H-1,2,4-triazol-1-ylmethyl compound, m.p. 99-100°. Continued elution with ethyl acetate-acetonitrile 80:20 provided a small amount of the title compound as a colorless solid: 15 130-133°C; nmr (CDCl<sub>3</sub>) 0.4 (6H, s), 3.7 (2H, s),

7.2-7.7 (9H, m), 7.9 (2H, s); microanalysis for  $C_{17}H_{19}N_3Si$  (mw 293.43):

Calculated: C, 69.58; H, 6.53; N, 14.32. Found: C, 69.0; H, 6.7; N, 13.9.

6.7; 14.2. 69.3:

25

20

Preparation of Dimethyl(phenyl)(1H-1,2,4-triazol-1-yl-methyl)silane

A mixture of 9.0 ml (9.2 g, 0.050 mol) of chloromethyldimethylphenylsilane and 5.5 g (0.060 mol) of 1,2,4-triazole sodium salt in 25 ml of dimethylformamide was stirred and warmed to 90-95°C for 2 hours, cooled, diluted with water, and extracted with ether. The ether solution was washed with water and brine, dried over magnesium sulfate, and evaporated to leave 8.1 g (75%) of a pale brown oil, n<sub>D</sub><sup>22</sup> 1.5350, containing the title compound and minor impurities as judged by nmr. A purer sample was obtained by distillation: bp 99° (0.02 mm); n<sub>D</sub><sup>20</sup> 1.5403; nmr (CDCl<sub>3</sub>)

15 0.4 (6H, s), 3.8 (2H, s), 7.2-7.7 (5H, m), 7.7 (1H, s), 7.8 (1H, s); analysis for C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>Si (mw 217.34):

Calculated C, 60.78; H, 6.96; N, 19.33; Found C, 60.7; H, 7.0; N, 16.9; 60.2; H, 7.0; N, 16.8.

25

20

Preparation of (4-Chlorophenyl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane

A mixture of 2.2 g (0.010 mol) of chloromethyl(4
chlorophenyl)dimethylsilane and 1.1 g (0.012 mol) of
1,2,4-triazole sodium salt in 5 ml of dimethylformamide was warmed to 80-90° for 2 hours, diluted with
water, and extracted with ether. The ether solution
was washed with water and brine, dried over magnesium

sulfate, and evaporated to leave 2.1 g (83%) of the
title compound as a yellow liquid: n<sub>D</sub><sup>21</sup> 1.5428;
ir (neat) 1555, 1470, 1245, 1130, 1080, 1010, 835,
805, 795, 735 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.4 (6H, s), 3.8
(2H, s), 7.4 (4H, broad s), 7.8 (1H, s), 7.9 (1H, s).

15

#### Example 23

Preparation of (2,4-Dichlorophenyl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane

A mixture of 5.1 g (0.020 mol) of chloromethyl
(2,4-dichlorophenyl)dimethylsilane and 2.0 g (0.022 mol) of 1,2,4-triazole sodium salt in 10 ml of dry dimethylformamide was stirred at 80-90° for 2 hours. The resulting slurry was cooled, diluted with water, and washed with ether. The ether extracts were washed with several portions of water and once with brine, dried over magnesium sulfate, and evaporated to leave 4.6 g (81%) of the title compound as a pale yellow liquid: n<sub>0</sub><sup>23</sup> 1.5580; ir (neat) 1550, 1485, 1440, 1345, 1260, 1240, 1130, 1085, 1025, 1005, 835 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.5 (6H, s), 4.1 (2H, s), 7.2-7.5 (3H, m), 7.8 (1H, s), 7.9 (1H, s).

Preparation of bis(4-Chlorophenyl)methyl(1H-1,2,4-triazol-1-ylmethyl)silane

A mixture of 6.3 g (0.020 mol) of chloromethylbis(4-chlorophenyl)methylsilane and 2.0 g (0.022 mol)
of 1,2,4-triazole sodium salt in 10 ml of dry dimethylformamide was stirred at 80°C for 4 hours. The resulting slurry was cooled, diluted with water, and washed
with ether. The ether extracts were washed with

several portions of water and once with brine, dried
over magnesium sulfate, and evaporated to leave 5.4 g
of yellow oil. Kugelrohr distillation at 120-150°
(airbath)/0.05 mm gave 4.0 g (58%) of the title compound as a pale yellow oil: n<sub>D</sub><sup>26</sup> 1.5966; nmr (CDCl<sub>3</sub>)

15 0.7 (3H, s), 4.1 (2H, s), 7.2-7.5 (8H, m), 7.8 (1H,
s), 7.9 (1H, s).

Preparation of bis(4-Fluorophenyl)methyl(1H-1,2,4-triazol-1-ylmethyl)silane

A mixture of 4.2 g (0.015 mol) of (chloromethyl)
bis(4-fluorophenyl)methylsilane and 1.4 g (0.015 mol)

of 1,2,4-triazole sodium salt in 8 ml of dimethylformamide was stirred at 80° for 2 hours. The resulting
slurry was cooled, diluted with water, and worked up
as in Example 24 to give 4.0 g of a pale yellow oil.

Impurities were removed by Kugelrohr distillation at
120-125° (0.05 mm), leaving behind 2.3 g (49%) of the
title compound as a yellow oil: n<sub>D</sub><sup>21</sup> 1.5538; ir (neat)
3065, 3030, 2960, 2925, 1590, 1500, 1270, 1235, 1165,
1110, 1010, 830, 790 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>): 0.7 (3H, s),
4.2 (2H, s), 7.1 (4H, t, J = 9), 7.5 (4H, d of d,
J = 6 and 9), 7.8 (1H, s) and 7.9 (1H, s).

By applying the procedures of Examples 19 and 21-25 to appropriate chloromethylsilanes, the compounds of Table VI in which  $Q_1=Q_2=H$  can be prepared.

25

#### Table VI

5

 $CH_3 CH_3 n_D^{23} 1.4626$ n-C12H25 CH3 CH3 n-C<sub>14</sub>H<sub>29</sub>  $CH_3 CH_3 n_D^{21} 1.4597$ n-C<sub>18</sub>H<sub>37</sub> CH<sub>3</sub> CH<sub>3</sub> cyclopropyl cyclobutyl CH3 CH3 cyclopentyl  $CH_3 CH_3 n_D^{22} 1.4906$ cyclohexyl 20  $CH_3$   $CH_3$   $n_D^{23}$  1.6051 1-naphthy1 CH3 CH3 2-naphthy1  $CH_3 \quad CH_3 \quad n_D^{20} \quad 1.5647$ 4-bromophenyl CH<sub>3</sub> CH<sub>3</sub> bp 108° (0.2 mm) 4-fluorophenyl 25  $CH_3 CH_3 n_0^{26} 1.5401$ 4-methoxyphenyl  $CH_3 CH_3 n_0^{22} 1.5754$ 4-phenoxyphenyl  $CH_3$   $CH_3$   $n_0^{22}$  1.5703 4-(4-chlorophenoxy)phenyl CH3 CH4 4-(4-fluorophenoxy)phenyl 30 4-(4-trifluoromethylphenoxy)phenyl CH3 CH3 4-(4-methylphenoxy)phenyl CH<sub>3</sub> CH<sub>3</sub>  $CH_3 CH_3 n_D^{23} 1.5790$ 4-thiomethylphenyl CH<sub>3</sub> CH<sub>3</sub> n<sub>D</sub><sup>22</sup> 1.4909 4-trifluoromethylphenyl  $CH_3 CH_3 n_D^{21} 1.5350$ 35. 4-methylphenyl

55
Table VI (continued)

	<u>R</u> 1	R <sub>2</sub>	R <sub>3</sub>	
5	4-methylsulfonylphenyl 4-i-propylphenyl	СН <sub>3</sub>	сн <sub>3</sub> сн <sub>3</sub>	n <sub>D</sub> 1.5538
	4-t-butylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	$n_{\rm D}^{23}$ 1.5125
	4-cyclohexylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	nD 1.5235
10	4-trifluoromethoxyphenyl 4-(4-chlorophenyl)phenyl	сн <sub>3</sub>	сн <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.4768
15	4-(4-bromophenyl)phenyl 4-(4-methylphenyl)phenyl 4-(4-trifluoromethylphenyl)phenyl 4-(4-fluorophenyl)phenyl	сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub>	сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub>	n <sub>0</sub> <sup>22</sup> 1.5802
	3-phenylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	$n_0^{21}$ 1.5939
	3-trifluoromethylphenyl 3-chlorophenyl	сн <sub>3</sub>	сн <sub>3</sub>	•
20	2-trifluoromethylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	$n_{\rm D}^{23}$ 1.4964
	2-phenylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	$n_0^{22}$ 1.5900
	2-chlorophenyl	CH <sub>3</sub>	СH <sub>3</sub>	$n_{\rm D}^{22}$ 1.5442
25	2-methoxyphenyl 2,3-dimethylphenyl	сн <sub>3</sub>	сн <sub>3</sub>	$n_{D}^{21}$ 1.5216
30	2,3-dimethoxyphenyl 2,4-difluorophenyl 2-fluoro-4-chlorophenyl 2-chloro-4-fluorophenyl 2-chloro-4-phenylphenyl 2-fluoro-4-phenylphenyl 2-methyl-5-chlorophenyl	сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub>	сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub>	n <sub>0</sub> <sup>22</sup> 1.5322
35	<pre>2,6-dimethoxyphenyl 2,6-dimethylphenyl</pre>	CH <sub>3</sub>	CH <sub>3</sub>	n <sub>D</sub> <sup>23</sup> 1.5404

	<u>R<sub>1</sub></u>	R <sub>2</sub>	R <sub>3</sub>	
5	3,4-dichlorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	$n_0^{22}$ 1.5602
	3-methyl-4-fluorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	47 40A
	3,5-dichlorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	m.p. 63-69°
	C2H5	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	
	i-C3H7	cyclohexyl	.CH <sub>3</sub>	
10	n-CaH9	<u>n</u> -C4H9	CH <sub>3</sub>	$n_{\rm D}^{22}$ 1.4672
10	, ,	cyclopropyl	CH <sub>3</sub>	J
	<u>n</u> -c <sub>10</sub> H <sub>21</sub> <u>n</u> -c <sub>12</sub> H <sub>25</sub>	<u>n</u> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	
		<u>i</u> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	
	- 14 23	3-methylbutyl	CH <sub>3</sub>	
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	n-C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	
15	cyclopropyl	cylopentyl	CH <sub>3</sub>	
	cyclopentyl cyclohexyl	cyclohexyl	CH <sub>3</sub>	
	1-naphthy1	n-CaH9	CH <sub>3</sub>	
	1-naphthy1	±-C <sub>Δ</sub> H <sub>9</sub>	CH <sub>3</sub>	
	2-naphthyl	<u>n</u> -C <sub>5</sub> H <sub>11</sub>	CH <sub>3</sub>	
20			CH <sub>3</sub>	-
	phenyl .	<u>n</u> -C <sub>3</sub> H <sub>7</sub>	_	$n_{\rm D}^{21}$ 1.5297
	phenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	CH <sup>2</sup>	<sup>11</sup> D 1.3237
	pheny1	1,1-dimethylpropyl	CH <sub>3</sub>	
	phenyl	<u>r</u> -c <sup>6</sup> H3	сн <sub>3</sub>	
25	4-phenylphenyl	<sup>C</sup> 2 <sup>H</sup> 5	CH <sub>3</sub>	20
	4-phenylphenyl	<u>n-</u> C4H9	CH <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.5838
	4-bromophenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	. сн <sub>3</sub>	
	4-chlorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	n <sub>D</sub> 1.5344
30		<u>n</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	$n_D^{22}$ 1.5120
,	4-fluorophenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	U
	4-phenoxyphenyl	cyclopropyl	CH <sub>3</sub>	
	4-i-propylphenyl	<u>i</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	
	4-t-butylphenyl		CH <sub>3</sub>	
35	3-phenylphenyl	<u>i</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	
,,	3—trifluoromethylphenyl	<sup>1</sup> ≥ − 4 ⊓ 9	3	

	<u>R<sub>1</sub></u>	R <sub>2</sub>	R <sub>3</sub>	
5	3-chlorophenyl	<u>n-</u> C5H11	CH <sub>3</sub>	
	2-methoxyphenyl	t-CaH9	CH <sub>3</sub>	
	2-thiomethylphenyl	cyclobutyl	CH <sub>3</sub>	
	2-phenylphenyl	<u>i</u> -C <sub>4</sub> H <sub>9</sub>	. сн <sub>3</sub>	
	2,4-dichlorophenyl	<u>n</u> -C4H9	CH <sub>3</sub>	.n <sub>D</sub> 1.5411
1Ó	2,4-dichlorophenyl	cyclopropyl	CH <sub>3</sub>	
10	2,3—dimethylphenyl	n-c3H7	сн <sub>3</sub>	
	2-methy1-5-fluorophenyl	cyclopentyl	CH <sub>3</sub>	
	2,5-dimethoxyphenyl	4-methylpentyl	CH <sub>3</sub>	
·	2,6-dimethylphenyl	l-methylbutyl	· CH <sub>3</sub>	
15	3,4-dichlorophenyl	n-C5H11	CH <sub>3</sub>	
17	3,5-dichlorophenyl	n-C4H9	CH <sub>3</sub>	
	3,5-dichlorophenyl	cyclohexyl	сн <sub>3</sub>	
	3-methyl-4-chlorophenyl	cyclopropyl	CH <sub>3</sub>	
	phenyl	phenyl	CH <sub>3</sub>	$n_0^{22}$ 1.5852
20	4-fluorophenyl	phenyl	CH <sub>3</sub>	$n_0^{20}$ 1.5718
	4-chlorophenyl	phenyl	CH <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.5926
	4-bromophenyl	phenyl	CH <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.6076
	4-phenylphenyl	phenyl	CH <sub>3</sub>	$n_{D}^{21}$ 1.6328
25	4-t-butylphenyl	phenyl	CH <sub>3</sub>	
	4-thiomethylphenyl	phenyl.	CH <sub>3</sub>	
	4-phenoxyphenyl	phenyl	CH <sub>3</sub>	
	4-trifluoromethoxyphenyl	pheny1	CH <sub>3</sub>	
•	4-methylsulfonylphenyl	phenyl	CH <sub>3</sub>	
30	4-cyclohexylphenyl	pheny1	CH <sub>3</sub>	
	4-(4-fluorophenyl)phenyl	phenyl	CH <sub>3</sub>	
	3—trifluoromethylphenyl	pheny1	CH <sub>3</sub>	20
	2-chlorophenyl	phenyl	CH <sub>3</sub>	n <sub>D</sub> <sup>20</sup> 1.5742
35	2-methoxyphenyl	phenyl	CH <sub>3</sub>	
1				

	$\frac{R_1}{R_1}$	<u>R</u> 2	<u>R3</u>	
5	2,4-dichlorophenyl	phenyl	CH <sub>3</sub>	$n_{\rm D}^{23}$ 1.5941
)	2-chloro-4-phenylphenyl	phenyl	CH <sub>3</sub>	J
	2-fluoro-4-phenylphenyl	phenyl _	CH <sub>3</sub>	
	3,5-dichlorophenyl	phenyl	СНŽ	•
	2,5-dimethoxyphenyl	phenyl	CH <sub>3</sub>	
10	2,6-dimethoxyphenyl	phenyl	CH <sub>3</sub>	
10	4-bromophenyl	4-bromophenyl	CH <sub>3</sub>	$n_{\rm D}^{21}$ 1.6245
	4-phenylphenyl	4-phenylphenyl	CH <sub>3</sub>	m.p. 42-46°
	4-methoxyphenyl	4-methoxyphenyl	CH <sub>3</sub>	$n_{\rm D}^{21}$ 1.5890
	3-trifluoromethylphenyl	3-trifluoromethylphenyl	CH <sub>3</sub>	J
15	2-chlorophenyl	2-chlorophenyl	CH <sub>3</sub>	$n_D^{21}$ 1.5965
	2-methoxyphenyl	2-methoxyphenyl	CH <sub>3</sub>	
·	2,4-dichlorophenyl	2,4-dichlorophenyl	CH <sub>3</sub>	$n_{\rm D}^{22}$ 1.6009
	3,5-dichlorophenyl	3,5-dichlorophenyl	CH <sub>3</sub>	
20	2-chlorophenyl	4-chlorophenyl	CH <sub>3</sub>	$n_{\rm D}^{20}$ 1.5918
	2-chlorophenyl	4-fluorophenyl	CH <sub>3</sub>	
	4-phenylphenyl	4-chlorophenyl	CH <sub>3</sub>	
	4-phenylphenyl	4-fluorophenyl	CH <sub>3</sub>	
	4-phenylphenyl	2,4-dichlorophenyl	CH <sub>3</sub>	
25	4-fluorophenyl	2,4-dichlorophenyl	CH <sub>3</sub>	
	4-chlorophenyl	2,4-dichlorophenyl	CH <sub>3</sub>	
	l-naphthyl	2,6-dimethoxyphenyl	CH <sub>3</sub>	
	4-phenoxyphenyl	3,4-dichlorophenyl	CH <sub>3</sub>	
	с <sub>2</sub> н <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	
30	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	<u>i</u> -c <sub>3</sub> H <sub>7</sub>	<u>i</u> -C <sub>3</sub> H	7
	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	n-C <sub>4</sub> H	
	<u>n</u> -C <sub>8</sub> H <sub>17</sub>	C2H5		pentyl
	<u>n</u> -C <sub>14</sub> H <sub>29</sub>	cyclopropyl		hylbutyl
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	<u>n</u> -C <sub>6</sub> H <sub>13</sub>	<u>r</u> -c6 <sub>H</sub>	
35	cyclopropyl	C <sub>2</sub> H <sub>5</sub>	<u>s-</u> C <sub>4</sub> H	9

	<u>R<sub>1</sub></u>	<u>R2</u>	R <sub>3</sub>
	cyclohexyl	<u>n-C<sub>3</sub>H<sub>7</sub> .</u>	n-C3H7
5	l-naphthyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	n-C4H9
	2-naphthyl .	n-CAH9	cyclobutyl
	pheny1	cyclopropyl	<u>n</u> -c <sub>6</sub> H <sub>13</sub>
	4-phenylphenyl	C <sub>2</sub> H <sub>5</sub>	C2H5
	4-phenylphenyl	n-C4H9	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
10	4-phenylphenyl	n-C6H13	n-C6H <sub>13</sub>
	4-phenylphenyl	cyclohexyl -	cyclohexyl
	4-chlorophenyl	n-CAH9	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
	4-fluorophenyl	n-C <sub>3</sub> H <sub>7</sub>	n-C <sub>3</sub> H <sub>7</sub>
	4-phenoxyphenyl	n-C4H9	cyclohexyl .
15	4-(4-chlorophenoxy)phenyl	n-C4H9	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
	4- <u>t</u> -butylphenyl	<u>s</u> -C <sub>4</sub> H <sub>9</sub>	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
	3-methoxyphenyl	C2H5	t-C4H9
	3-trifluoromethylphenyl	<u>s</u> -C <sub>4</sub> H <sub>9</sub>	<u>s</u> -C4H9
	2-thiomethylphenyl	<u>1</u> -C <sub>3</sub> H <sub>7</sub>	3-methylbutyl
20	2-phenylphenyl	cyclohexyl	cyclohexyl
	2,4-dichlorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>n</u> -C4H9
	2,6-dimethylphenyl	t-C4H9	t-C4H9
	3,5-dichlarophenyl	cyclopentyl	cyclopentyl
	3-methyl-4-chlorophenyl	<u>s</u> -C4H9	<u>s</u> -C <sub>4</sub> H <sub>9</sub>
25	2-methyl-5-fluorophenyl	<u>n</u> -C4H9	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
	С <sub>2</sub> Н <sub>5</sub>	phenyl	phenyl
	cyclohexyl	phenyl	phenyl
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	phenyl	phenyl ·
	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	4-chlorophenyl	4-chlorophenyl
30	<u>n</u> -C <sub>12</sub> H <sub>25</sub>	4-chlorophenyl	4-chlorophenyl
	l-naphthyl	4-fluorophenyl	4-fluorophenyl
	cyclopropyl	phenyl	4- <u>t</u> -butylphenyl
	<u>n-</u> C <sub>4</sub> H <sub>9</sub>	phenyl	4-phenylphenyl
7.5	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	phenyl	2,4-dichlorophenyl
35	<u>n-C3H7</u>	phenyl	3-trifluorometnylphenyl

	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub> .		
5	<u>i</u> -C <sub>u</sub> H <sub>9</sub>	phenyl	3,5-dichlorophenyl 2,6-dimethoxyphenyl 2-fluorophenyl		
	cyclopentyl	phenyl			
	n-C <sub>14</sub> H <sub>29</sub>	4-chlorophenyl			
	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	4-fluorophenyl	4-phenylphenyl		
	phenyl	phenyl	phenyl m.p. 118-121°		
10	4-chlorophenyl	4-chlorophenyl	4-chlorophenyl		
	4-fluorophenyl	4-fluorophenyl	4-fluorophenyl		
	4-phenylphenyl	4-phenylphenyl	4-phenylphenyl		
	2,4-dichlorophenyl	2,4-dichlorophenyl	2,4-dichlorophenyl		
15	phenyl	4-fluorophenyl	4-fluorophenyl		
	phenyl .	4-chlorophenyl	4-chlorophenyl		
	phenyl	4-phenylphenyl	4-phenylphenyl		
	phenyl	2,4-dichlorophenyl	2,4-dichlorophenyl		
	2-naphthyl	4-methylthiophenyl	4-methylthiophenyl		
20	4-chlorophenyl	2-methoxyphenyl	2-methoxyphenyl		
	4-chlorophenyl	3-chlorophenyl	3-chlorophenyl		
	phenyl	2-chlorophenyl	4-fluorophenyl		
	phenyl	4-chlorophenyl	4-phenylphenyl		
	l-naphthyl	4-bromophenyl	3-methylphenyl		
	4-phenoxyphenyl	3,5—dimethylphenyl	3,4-dichlorophenyl		

Preparation of (3,5-Dimethyl-1H-1,2,4-triazol-1-yl-methyl)[bis(4-fluorophenyl)]methylsilane

The title compound is prepared by applying the procedure of Example 25 to equimolar quantities of chloromethyl[bis(4-fluorophenyl)]methylsilane and 3,5-dimethyl-1,2,4-triazole sodium salt.

Related compounds may be made by substituting salts of 3-methyl-1,2,4-triazole for the 3,5-dimethyl-triazole salt.

#### Example 27

Preparation of (1,1'-Biphenyl-4-yl)dimethyl(3-methyl-1H-1,2,4-triazol-1-ylmethyl)silane

A solution of 5.9 q (0.020 mol) of (1,1'-bi-15 phenyl-4-yl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane in 40 ml of dry tetrahydrofuran was chilled to -40° under  $N_2$  and stirred while 12.5 ml (0.020 mol) of 1.6 molar n-butyllithium in hexane was added dropwise. The resulting yellow solution was stirred another 15 minutes at -40°, treated with 1.9 ml (4.2 g, 0.030 mol) of methyl iodide, and allowed to warm to room temperature. The resulting solution was diluted with water and extracted with hexanes. Washing the organic extracts with water and brine, drying over magnesium sulfate, and evaporation gave 5.7 g of solid, which was purified by dry-column chromatography over silica gel (ethyl acetate elution) to give 1.1 g of crude product. Recrystallization from 12 ml of 3:1 hexanesethyl acetate then gave 0.97 g (16%) of the title compound as an off white solid: m.p. 95-98°; ir (Nujol<sup>R</sup>) 1590, 1270, 1250, 1180, 1120, 830, 765, 700 cm<sup>-1</sup>; nmr  $(CDCl_3)$  0.5 (6H, s), 2.2 (3H, s), 3.7 (2H, s), 7.2-7.7 (9H, m), 7.8 (1H, s).

Although the indicated structure is preferred for steric reasons, the position of the methyl group on the triazole ring has not been proven, and it is possible that the product is (1,1'-biphenyl-4-yl)-dimethyl(5-methyl-1H-1,2,4-triazol-1-ylmethyl)silane.

The procedures of Examples 26 and 27 may be used to prepare the compounds of Table VII.

#### Table VII

 $\begin{array}{c} R_{2} \\ R_{1}-Si-CH_{2}N \\ R_{3} \end{array}$ 

5

10 cyclohexyl CH3 l-naphthyl  $CH_3$ CH3 phenyl CH 15 Н pheny1 CH CH~ СН CH 4-phenylphenyl CH CH3 CH<sub>3</sub> 4-(4-fluorophenyl)phenyl CH<sub>3</sub> CH CH<sub>3</sub> 4-phenoxyphenyl CHZ CH3 3-trifluoromethylphenyl CH 20  $CH_3$ CH<sub>3</sub> 2-methoxyphenyl CH3  $CH_3$ CH3 CHZ 2,4-dichlorophenyl CH<sub>3</sub> CH  $CH_3$ 2-chloro-4-phenylphenyl CH<sub>3</sub> CH<sub>3</sub> n-CAH9 CHZ phenyl CH3 CH<sub>3</sub> Н 4-phenylphenyl n-CAHo CH<sub>3</sub> 25 CH CH 2,4-dichlorophenyl n-C6H13 ದ್ನ cyclohexyl CH CH 4-(4-chlorophenoxy)phenyl pheny1 CHZ Н CHpheny1 CH3 CHZ CHZ 4-fluorophenyl phenyl CH3 CHZ 4-fluorophenyl pheny1 30  $CH_3$ phenyl CH Н 4-chlorophenyl 4-fluorophenyl 4-fluorophenyl CH<sub>~</sub> Н CH3 CHZ 4-fluorophenyl ದಿಗ್ನ Н 4-fluorophenyl 4-chlorophenyl CH3 4-chlorophenyl CH<sub>3</sub> 4-chlorophenyl 떡 CH-4-chlorophenyl 35 CH<sub>3</sub> 2-chlorophenyl 4-chlorophenyl CH<sub>3</sub>

Table VII (continued)

	<u>R_1</u>	<u>R2</u>	R <sub>3</sub>	$\frac{q_1}{q_1}$	$\frac{Q_2}{2}$
5	2,4-dichlarophenyl	2,4-dichlorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
•	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	<u>n</u> -c <sub>6</sub> H <sub>13</sub>	n-C6H13	CH <sub>3</sub>	CH <sub>3</sub>
	1-naphthyl	n-C4H9	n-C4H9	Н	CH <sub>3</sub>
	phenyl	phenyl	phenyl	Н	CH <sub>3</sub>
	phenyl	phenyl	phenyl	CH <sub>3</sub>	Н
10	ohenvl	phenyl	pheny1	CH <sub>3</sub>	CH <sub>3</sub>

Preparation of the 1:1 complex of (1,1'-8ipheny1-4-y1)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane and Cuprous Chloride

A mixture of 5.0 g (0.017 mol) of (1,1'-biphenyl-4-y1)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane and 1.7 g (0.017 mol) of cuprous chloride in 170 ml of tetrahydrofuran was refluxed under  ${\rm N_2}$  for 30 minutes, and the resulting deep green solution was evaporated 10 to leave the title compound as a dark greenish-brown solid: m.p. 85-90°; ir (Nujol<sup>R</sup>) 3110, 1590, 1280, 1250, 1120, 1010, 990, 840, 825, 760, 700 cm<sup>-1</sup>.

The following metal complexes of (1,1'-biphenyl-4-yl)dimethyl(lH-1,2,4-triazol-4-ylmethyl)silane were prepared similarly:

- 1:1 Complex with cupric chloride: m.p. 83-87°
- 2:1 Complex with cupric chloride: m.p. 85-92°
- 1:1 Complex with zinc chloride:  $n_{\Omega}^{21}$  1.5737
- 1:1 Complex with manganous sulfate: m.p. 244-250° (decomp.)

20

25

5

#### Example 29

Preparation of the 4-Dodecylbenzenesulfonate Salt of (1,1'-8iphenyl-4-yl)dimethyl(1H-1,2,4-triazol-1-yl-1)methyl)silane

A solution of 1.0 g (0.0034 mol) of (1,1'-biphenyl-4-yl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane in 10 ml of dichloromethane was combined with a solution of 1.1 g (0.0034 mol) of 4-dodecylbenzenesulfonic acid in 10 ml of dichloromethane. The resulting solution was evaporated to leave the title salt as a viscous yellow oil:  $n_0^{20}$  1.5645; ir (neat) 3110, 3050, 3020, 2960, 2920, 2850, 2570, 1920, 1600, 1545, 1485, 1455, 1405, 1250, 1225, 1165, 1120, 1030, 1010, 990, 845, 825, 755, 735, 700, 670, 635  $cm^{-1}$ .

Preparation of the 2:1 complex of [bis(4-Fluorophenyl)]methyl(lH-1,2,4-triazol-1-ylmethyl)silane and Cupric Chloride

A mixture of 1.0 g (0.0032 mol) of [bis(4-fluorophenyl)]methyl(lH-1,2,4-triazol-1-ylmethyl)silane and 0.2 g (0.0016 mol) of cupric chloride in 30 ml of tetrahydrofuran was refluxed under  $N_2$  for 30 minutes and evaporated to leave the title complex as a blue-10 green glass: no distinct m.p.; ir (Nujol<sup>R</sup>) 1580, 1490, 1230, 1160, 1110, 830, 785 cm<sup>-1</sup>.

The 1:1 complex with cuprous chloride was prepared similarly to give a dark green glass: no distinct m.p.; ir as above.

By applying the procedures of Examples 26-28, any of the compounds of Tables VI, VII, VIII, IX, XII and XIII can be converted to salts or metal complexes.

#### Example 31

Preparation of (1,1-'Biphenyl-4-yl)(1H-1,2,4-triazol-20 1-ylmethyl)(methoxy)methylsilane

A mixture of (1,1'-biphenyl-4-yl)chlorochloromethylmethylsilane and two equivalents of 1,2,4-triazole sodium salt in dimethylformamide is warmed to 80-90°C for 2 hours. Ten equivalents of methanol is then added, and the mixture is held at 70°C for 1 hour, cooled, diluted with water, and quickly extracted with ether. Washing the ether solution with water and brine, drying over magnesium sulfate, and evaporation leaves the title compound.

Related compounds can be made in the same way, using the appropriate chlorosilane and alcohol; for  $R_6 = OH$ , water is used instead of an alcohol, and hydrolysis is conducted at 20-25°C instead of 70°.

30

25

5

Preparation of (1,1-dimethylethoxy)methyl(phenyl)(1H-1,2,4-triazol-l-ylmethyl)silane

A mixture of 3.6 g (0.015 mol) of chloromethyl-5 (1,1-dimethylethoxy)methyl(phenyl)silane and 1.3 g (0.015 mol) of 1,2,4-triazole sodium salt in 8 ml of dimethylformamide was stirred at 80° for 2 hours, cooled, and poured onto water. The resulting mixture was extracted with ether, and the ether extracts were 10 washed with water and brine, dried over magnesium sulfate, and evaporated to leave 2.7 g of a yellow oil. Chromatography on silica gel, eluting with 50:50 ethyl acetate-hexanes, provided 1.5 g (36%) of the title compound as a pale yellow oil:  $n_0^{21}$  1.5134; ir (neat) 15 3120, 3070, 3045, 2975, 2925, 1500, 1425, 1380, 1365, 1270, 1255, 1240, 1190, 1140, 1115, 1050, 1020, 1010, 830, 810, 790, 740, 700, 680 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>): 0.6 (3H, s), 1.3 (9H, s), 3.9 (2H, s), 7.3-7.7 (5H, m), 7.9 (1H, s) and 8.0 (1H, s).

The compounds of Table VIII and IX in which  $Q_1=Q_2=H$  can be made using the procedures of Examples 31 and 32.

25

#### Table VIII

R<sub>1</sub>-Si-CH<sub>2</sub>N N

5

Ŗ<sub>6</sub> CH<sub>3</sub> CH-3 t-CAH9 CH-10 С<sub>2</sub>Н<sub>5</sub> СН<sub>3</sub> CH<sub>3</sub> C2H5 CH<sub>3</sub> n-C6H13 s-C4H9 CH<sub>3</sub> cyclopropyl CH<sub>3</sub> CH<sub>3</sub> cyclohexyl 15 i-C3H7 i-C3H7 1-naphthyl cyclobutyl 2-naphthy1 CH<sub>3</sub> phenyl CH<sub>3</sub> CH3 phenyl C2H5 CH<sub>3</sub> phenyl 20 i-C<sub>3</sub>H<sub>7</sub> CH<sub>3</sub> phenyl Н t-CAH9 phenyl CH<sub>3</sub> <u>n</u>-C<sub>4</sub>H<sub>9</sub> 4-phenylphenyl Н t-CaH9 4-phenylphenyl C2H5 CH3 25 4-phenylphenyl n-C4H9 CH3 4-phenylphenyl n-C4H9 n-C4H9 4-chlorophenyl CH<sub>3</sub> CH<sub>3</sub> 4-chlorophenyl C2H5 CH3 4-chlorophenyl n-C3H7 n-C6H13 30 4-fluorophenyl C2H5 CH<sub>3</sub> 4-fluorophenyl <u>i</u>-C<sub>4</sub>H<sub>9</sub> cyclohexyl 4-phenoxyphenyl <u>s</u>-C<sub>4</sub>H<sub>9</sub> n-C3H7 4-t-butylphenyl Н 3-trifluoromethylphenyl t-C4H9 C<sub>2</sub>H<sub>5</sub> cyclopentyl 2-methylthiophenyl 35

	<u>R</u> 1	<u>R2</u> .	<u>R<sub>6</sub></u>
	2,4-dichlorophenyl	CH <sub>3</sub>	CH <sub>3</sub>
5	2,4-dichlorophenyl	CH	C <sub>2</sub> H <sub>5</sub>
	2,4-dichlorophenyl	CH <sub>3</sub>	t-C4H9
	2,4-dichlorophenyl	n-CaHo	с <sub>2</sub> н <sub>5</sub>
	2,3-dimethylphenyl	cyclopropyl	<u>i</u> -c <sub>3</sub> H <sub>7</sub>
10	2-methyl-5-fluorophenyl	<u>s</u> -C <sub>1</sub> H <sub>9</sub>	n-C3H7
	2,6-dimethoxyphenyl	l,l-dimethylpropyl	Н
	3-methyl-4-chlorophenyl	C <sub>2</sub> H <sub>5</sub>	CH3
	3,5-dichlorophenyl	<u>n</u> -C <sub>5</sub> H <sub>11</sub>	C2H5
	<u>n</u> -C <sub>12</sub> H <sub>25</sub>	2,4-dichlorophenyl	t-C4H9
15	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	phenyl	CH <sub>3</sub>
15	1-naphthyl	phenyl	C2H5
	phenyl	phenyl	t-C4H9
	4-fluorophenyl .	phenyl	CH <sub>3</sub>
20	4-chlorophenyl	phenyl	D-C3H7
	4-phenylphenyl	phenyl	C2H5
20	4-phenylphenyl	phenyl	<u>s</u> -C4H9
	4-t-butylphenyl	phenyl	<u>s</u> -C4H9
	3-fluorophenyl	pheny1	C2H5
	2-methoxyphenyl	phenyl	Н
	2-chlorophenyl	phenyl	CH <sub>3</sub> .
25	2,4-dichlorophenyl	pheny1	<u>i</u> -C <sub>3</sub> H <sub>7</sub>
	3,5-dichlorophenyl	phenyl	n-C3H7
	4-fluorophenyl	4-fluorophenyl	<u>t</u> -C4H9
	4-fluorophenyl	4-fluorophenyl	C2H5
30	4-chlorophenyl	4-chlorophenyl	CH <sub>3</sub>
	4-chlorophenyl	4-chlorophenyl	C <sub>2</sub> H <sub>5</sub>
	4-phenylphenyl	4-phenylphenyl	CH <sub>3</sub>
	2,4-dichlorophenyl	2,4-dichlorophenyl	с <sub>2</sub> н <sub>5</sub>
	3-trifluoromethylphenyl	3-trifluoromethylphenyl	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
<b>-</b> -	2-methoxyphenyl	2-methoxyphenyl	ü
35	2-chlorophenyl	4-fluorophemyi	•

# 70 Table VIII (continued)

R <sub>1</sub>	<u>R<sub>2</sub></u>	R <sub>6</sub>
3-trifluoromethylphenyl	4-t-butylphenyl	n-C4H9
2-fluoro-4-chlorophenyl	4-bromophenyl	<u>i</u> -c <sub>3</sub> H <sub>7</sub>
2,3-dimethylphenyl	4—methylthiophenyl	C <sub>2</sub> H <sub>5</sub>
2,6-dimethoxyphenyl	4-methoxyphenyl	Н
3,4-dichlorophenyl	4-methylphenyl	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
	3-trifluoromethylphenyl 2-fluoro-4-chlorophenyl 2,3-dimethylphenyl 2,6-dimethoxyphenyl	3-trifluoromethylphenyl 4-t-butylphenyl 2-fluoro-4-chlorophenyl 4-bromophenyl 2,3-dimethylphenyl 4-methylthiophenyl 2,6-dimethoxyphenyl 4-methoxyphenyl

71 Table IX

 $\begin{array}{c} \begin{array}{c} R_2 \\ R_1 - Si - CH_2 N \\ OR_6 \end{array} \end{array} \begin{array}{c} Q_1 \\ N \\ Q_2 \end{array}$ 

	<u>R<sub>1</sub></u>	R <sub>2</sub>	<u>R<sub>6</sub></u>	$\frac{Q_1}{Q_1}$	<u>Q</u> 2
	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
10	cyclohexyl	CH <sub>3</sub>	1-C3H7	н	CH <sub>3</sub>
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	n-C <sub>6</sub> H <sub>13</sub>	t-C4H9	CH <sub>3</sub>	CH <sub>3</sub>
	18'37 l-naphthyl	CH <sub>3</sub>	1-C3H7	CH <sub>3</sub>	CH <sub>3</sub>
	phenyl	сн <sub>3</sub>	t-C4H9	Н	CH <sub>3</sub>
	phenyl	CH <sub>3</sub>	t-C4H9	CH <sub>3</sub>	Н
15	phenyl	CH <sub>3</sub>	t-C4H9	CH <sub>3</sub>	CH <sub>3</sub>
	phenyl	CH <sub>3</sub>	<u>s-</u> C <sub>4</sub> H <sub>9</sub>	н	CH <sub>3</sub>
	phenyl	CHŽ	<u>i</u> -C4H9	Н	CH <sub>3</sub>
	4-phenylphenyl	<u>n-C4H9</u>	t-C4H9	Н	CH <sub>3</sub>
20	4-phenylphenyl	CH-z	t-C4H9	Н	CH <sub>3</sub>
	4-phenylphenyl	CHŽ	t-C4H9	CH <sub>3</sub>	CH <sub>3</sub>
	4-chlorophenyl	сн <sub>3</sub>	t-C4H9	Н	CH <sub>3</sub>
	4-chlorophenyl	CH <sub>3</sub>	<u>t</u> -C4H9	CH <sub>3</sub>	CH <sub>3</sub>
	4-fluorophenyl	CH <sub>3</sub>	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	Н	CH <sub>3</sub>
25	4-fluorophenyl	CH <sub>3</sub>	<u>t</u> -C4H9	CH <sub>3</sub>	CH <sub>3</sub>
25	phenyl	phenyl	<sup>C</sup> 2 <sup>H</sup> 5	CH <sub>3</sub>	CH <sub>3</sub>
	phenyl	phenyl	<u>n-C</u> 3H7	CH <sub>3</sub>	CH <sub>3</sub>
	4-fluorophenyl	phenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	H	CH <sub>3</sub>
	4-fluorophenyl	phenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	CH <sub>3</sub>
30	4-chlorophenyl	phenyl	<u>1</u> -C <sub>3</sub> H <sub>7</sub>	H	CH <sub>3</sub>
70	2,4-dichlorophenyl	phenyl	H	CH <sup>3</sup> .	CH <sub>3</sub>
	4-fluorophenyl	4-fluorophenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	Н	СН <sub>3</sub> Н
	4-fluorophenyl	4-fluorophenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	
	4-fluorophenyl	4-fluorophenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub> CH	CH <sub>3</sub>
35	2-methoxyphenyl	2-methoxyphenv1	5 C 2	H	
,,	3-methylphenyl	3-methylphenyl	<u>i</u> -C <sub>4</sub> H <sub>9</sub>	п	<sup>‡</sup> 3

# Preparation of Chloromethyl(dichloro)phenylsilane

A solution of 25.1 ml (36.8 g, 0.200 mol) of chloromethyltrichlorosilane in 400 ml dry tetrahydro
furan was cooled to -78° under nitrogen and stirred vigorously while 48.0 ml (0.100 mol) of 2.1 molar phenyllithium was slowly dripped in over 1 hour. After stirring another 30 minutes at -78° the solution was allowed to warm to room temperature and evaporated to about 200 ml. Addition of 500 ml ether, filtration to remove precipitated lithium chloride, and evaporation of the filtrate left 25.0 g of liquid. Distillation gave 6.5 g (29%) of the title compound as a colorless liquid: bp 62-82° (0.15 mm); nmr (CDCl<sub>3</sub>): 6 3.3 (s, 2) and 7.1-7.9 (m, 5).

#### Example 34

# Preparation of Chloromethyl(diethoxy)phenylsilane

A solution of 1.0 g (0.0044 mol) of chloromethyl(dichloro)phenylsilane in 8 ml of absolute ethanol was cooled to 0° under nitrogen and stirred while 0.61 ml (0.445 g, 0.0044 mol) of triethylamine was slowly added, giving a slurry that was allowed to warm to room temperature. Addition of 50 ml of ether, filtration to remove precipitated triethylamine/hydrochloride, and evaporation of the filtrate left a residue which was filtered through a short silica gel column (95% petroleum ether:ethyl acetate as the eluent) to give 0.80 (73%) of the title compound as a colorless oil: nmr (CDCl<sub>3</sub>): 1.25 (t, 6, J = 6Hz), 3.0 (s, 2), 3.9 (q, 4, J = 6Hz) and 7.2-7.9 (m, 5).

Preparation of Chloromethyl(phenyl)bis(2-propoxy)silane

A solution of 2.0 g (0.009 mol) of chloromethyl(dichloro)phenylsilane and 5 ml of 2-propanol in 15 ml

of dimethylformamide was stirred under N<sub>2</sub> while 2.5
ml (1.9 g, 0.018 mol) of triethylamine was added dropwise. The resulting slurry was warmed to 80° for 2
hours, cooled, diluted with water, and extracted with
ether. The ether extracts were washed with water and
brine, dried over magnesium sulfate, and evaporated to
leave 2.2 g of liquid. Column chromatography over
silica gel, eluting with petroleum ether, provided 1.4
g (58%) of the title compound as a colorless liquid:
n<sub>D</sub> (1.4741; nmr (CDCl<sub>3</sub>) 1.2 (12H, d, J = 6), 3.0 (2H,
s), 4.3 (2H, septet, J = 6), 7.3-7.8 (5H, m).

The compounds of Tables X and XI can be made using the procedures of Examples 33-35.

# 74 <u>Table X</u>

oR<sub>6</sub> R<sub>1</sub>-\$i-CH<sub>2</sub>Cl

	R <sub>1</sub>	R <sub>6</sub>
	C <sub>2</sub> H <sub>5</sub>	t-C4H9
10	n-CAH9	C2H5
	<u>n-C<sub>18</sub>H<sub>37</sub></u>	CH <sub>3</sub>
	cyclohexyl	<u>n-C3H7</u>
	1-naphthy1	<u>i</u> -C4H9
	phenyl	CH <sub>3</sub>
15	phenyl ·	<u>n-C</u> 3H7
	phenyl	<u>t</u> -C4H9
	4-phenylphenyl	<sup>C</sup> 2 <sup>H</sup> 5
	4-phenylphenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
	4-fluorophenyl	CH <sub>3</sub>
20	4-fluorophenyl	с <sub>2</sub> н <sub>5</sub>
	4-chlorophenyl	C <sub>2</sub> H <sub>5</sub>
	4-chlorophenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>
	3-trifluoromethylphenyl	<u>s</u> -C <sub>4</sub> H <sub>9</sub>
	2-methoxyphenyl	<u>n</u> -C <sub>3</sub> H <sub>7</sub>
25 <sup>-</sup>	2,3-dimethylphenyl	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
	2,4-dichlorophenyl	CH <sub>3</sub>
	2,4-dichlorophenyl	C <sub>2</sub> H <sub>5</sub>
	2-methoxy-5-fluorophenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>
	2,6-dimethoxyphenyl	CH <sub>3</sub>
30	3,4-dichlorophenyl	C <sub>2</sub> H <sub>5</sub>
	3,5-dichlorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>

3-trifluoromethylphenyl

# Table XI (continued)

	R <sub>1</sub>	<u>R<sub>6</sub></u>	
		<u>n-</u> C <sub>4</sub> H <sub>9</sub>	
5	2-methoxyphenyl	-cH <sub>2</sub> CH-	
	2,3-dimethylphenyl	-CH <sub>2</sub> CH <sub>2</sub> -	. •
		C <sub>2</sub> H <sub>5</sub>	
	2,4-dichlorophenyl	-сн <sub>2</sub> сн-	
		<u>n</u> -C <sub>3</sub> H <sub>7</sub>	
10	2,4-dichlorophenyl	-CH <sub>2</sub> CH-	•
		CH <sub>3</sub> CH <sub>3</sub>	•
	2-methoxy-5-fluorophenyl	-CHC(CH3)2CH-	
	2,6-dimethoxyphenyl	-CH <sub>2</sub> CH <sub>2</sub> -	
	•	CH <sub>3</sub> CH <sub>3</sub>	
15	3,4-dichlorophenyl	-CHCH2CH	
		CH <sub>3</sub> CH <sub>3</sub>	
	3,5—dichlorophenyl	-ČHČH-	
	C <sub>2</sub> H <sub>5</sub>	-CH_CH=CHCH <sub>2</sub> -	
		CH <sub>3</sub> CH <sub>3</sub>	
20	<u>п</u> –С <sub>18</sub> Н <sub>37</sub>	-CHCH2CH2CH-	
	· phenyl	-CH_CH=CHCH <sub>2</sub> -	
	phenyl	-c(cH <sub>3</sub> ) <sub>2</sub> cH=CHC(CH <sub>3</sub> ) <sub>2</sub> -	
		сн <sub>з</sub> сн <sub>з</sub> -ансн,сн,ан-	bp 57-60°.
25	phenyl	-c(cH <sub>3</sub> ) <sub>2</sub> cH <sub>2</sub> cH <sub>2</sub> c(cH <sub>3</sub> ) <sub>2</sub> -	(0.15 mm)
23	phenyl	-CH_CH=CHCH <sub>2</sub> -	
	4-phenylphenyl	CH <sub>3</sub> CH <sub>3</sub>	
	4-phenylphenyl	-CH <sub>2</sub> C==CCH <sub>2</sub> -	
	4-fluorophenyl	-CH <sub>2</sub> -CH=CHCH <sub>2</sub> -	
30	4-chlorophenyl	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	•
	4-01401001101172	2 2 2 2 n-c <sub>4</sub> H <sub>9</sub>	
	4-phenoxyphenyl	-CH2CH2CH2CH-	
	T prioritionly priority =	CH <sub>3</sub> . CH <sub>3</sub>	
	3-trifluoromethylphenyl	-CHCH=CHCH-	
35		CH <sub>3</sub> CH <sub>3</sub>	•
	2-methoxyphenyl	сн <sub>3</sub> сн <sub>3</sub> -сн <sub>2</sub> сн—снсн <sub>2</sub> -	

.

## Example 36

Preparation of Phenylbis(2-propoxy)(1H-1,2,4-triazol-1-ylmethyl)silane

The title compound can be made by applying the procedure of Example 32 to chloromethyl(phenyl)bis-(2-propoxy)silane:  $n_D^{22}$  1.4962; nmr (CDCl<sub>3</sub>) 1.1 (12H, d, J = 6), 4.0 (2H, s), 4.3 (2H, septet, J = 6), 7.2-8.0 (7H, m).

The compounds of Tables XII and XIII can be made similarly.

15

20

25

7.8 Table XII

R1-Si-CH<sub>2</sub>N N Q<sub>2</sub>

•				
10	R <sub>1</sub> C <sub>2</sub> H <sub>5</sub> <u>n</u> -C <sub>4</sub> H <sub>9</sub> <u>n</u> -C <sub>18</sub> H <sub>37</sub>	E-C4H9 C2H5 CH3	<u>Q</u> 1 н н	<del>Q</del> 2 н н
15	cyclohexyl 1-naphthyl phenyl phenyl phenyl phenyl phenyl	<u>n</u> -C <sub>3</sub> H <sub>7</sub> <u>i</u> -C <sub>4</sub> H <sub>9</sub> CH <sub>3</sub> <u>r</u> -C <sub>3</sub> H <sub>7</sub> <u>i</u> -C <sub>3</sub> H <sub>7</sub> <u>t</u> -C <sub>4</sub> H <sub>9</sub>	н сн <sub>3</sub> н сн <sub>3</sub>	H CH <sub>3</sub> CH <sub>3</sub> H
20	4-phenylphenyl 4-phenylphenyl 4-fluorophenyl 4-fluorophenyl 4-chlorophenyl	C <sub>2</sub> H <sub>5</sub> <u>r</u> -C <sub>4</sub> H <sub>9</sub> cH <sub>3</sub> C <sub>2</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	СН <sub>3</sub> Н Н Н Н	СН <sub>3</sub> Н Н Н
25	4-chlorophenyl 3-trifluoromethylphenyl 2-methoxyphenyl 2,3-dimethylphenyl 2,4-dichlorophenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub> <u>s</u> -C <sub>4</sub> H <sub>9</sub> <u>r</u> -C <sub>3</sub> H <sub>7</sub> <u>i</u> -C <sub>4</sub> H <sub>9</sub> cH <sub>3</sub>	H CH <sub>3</sub> H CH <sub>3</sub> H	н СН <sub>3</sub> СН <sub>3</sub> СН <sub>3</sub> н
30	2,4-dichlorophenyl 2-methoxy-5-fluorophenyl 2,6-dimethoxyphenyl 3,4-dichlorophenyl 3,5-dichlorophenyl	C <sub>2</sub> H <sub>5</sub> <u>i</u> -C <sub>3</sub> H <sub>7</sub> CH <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	 Н Н Н	н н н н

# Table XIII

5	R <sub>1</sub> -Si-CH <sub>2</sub> N <sub>N</sub>
	*2

	R <sub>1</sub>	<u>R<sub>6</sub></u>	$\frac{Q_1}{2}$	Q <sub>2</sub>
10	 c <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> CH <sub>2</sub> -	CH <sub>3</sub>	CH <sub>3</sub>
	<u>n-</u> C <sub>4</sub> H <sub>9</sub>	сн <sub>3</sub> -сн <sub>2</sub> сн-	н	CH <sub>3</sub>
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> - ,	Н	Н
15	cyclohexyl	с <sub>12</sub> н <sub>5</sub> -сн <sub>2</sub> сн-	Н	CH <sub>3</sub>
•	1-naphthy1	-CH <sub>2</sub> CH <sub>2</sub> -	CH <sub>3</sub>	Н
	phenyl	-CH <sub>2</sub> CH <sub>2</sub> -	CH <sub>3</sub>	CH <sub>3</sub>
20	phenyl	C <sub>2</sub> H <sub>5</sub> -CH <sub>2</sub> CH-	H	н
	phenyl	<u>л</u> -С <sub>3</sub> Н <sub>7</sub> -СН <sub>2</sub> СН-	н	Н
	phenyl	-C(CH3)2C(CH3)2-	Н	Н
	4-phenylphenyl	-CH <sub>2</sub> CH <sub>2</sub> -	Н	Н
25	4-phenylphenyl	С <sub>12</sub> Н <sub>5</sub> -СН <sub>2</sub> СН- СН <sub>3</sub> СН <sub>3</sub>	н	Н
	4-phenylphenyl	-cH—cH-	Н	н
	4-fluorophenyl	-CH2CH2-	Н	Н
30	4-fluorophenyl	сн <sub>з</sub> -сн <sub>2</sub> сн- с <sub>2</sub> н <sub>5</sub>	н	Н
	4-chlorophenyl	-CH <sub>2</sub> CH-	н	Н
	4-chlorophenyl	-c(CH <sub>3</sub> ) <sub>2</sub> c(CH <sub>3</sub> ) <sub>2</sub> -	н	н
35	3-trifluoromethylphenyl	сн <sub>э</sub> -снсн <sub>2</sub> с(сн <sub>3</sub> ) <sub>2</sub> -	CH <sub>Z</sub>	٠ ٣.

# Table XIII (continued)

	R <sub>1</sub>	<u>R<sub>6</sub></u>	$\frac{Q_1}{2}$	$\frac{Q_2}{2}$
-	•	n-C4H9		
5	2-methoxyphenyl	-CH2CH-	Н	CH <sub>3</sub>
	2,3-dimethylphenyl	-CH <sub>2</sub> CH <sub>2</sub> -	CH <sub>3</sub>	CH <sub>3</sub>
		C <sub>2</sub> H <sub>5</sub>	•	•
	2,4-dichlorophenyl	-CH2CH-	Н	Н
		<u>n-</u> C <sub>3</sub> H <sub>7</sub>		
10	2,4-dichlorophenyl	-CH <sub>2</sub> CH-	Н	Н
	<b>\$</b>	CH <sub>3</sub> CH <sub>3</sub>		
	2-methoxy-5-fluorophenyl	-CHC(CH <sub>3</sub> ) <sub>2</sub> CH-	Н	Н
	2,6-dimethoxyphenyl	-CH <sub>2</sub> CH <sub>2</sub> -	Н	Н
		CH <sub>3</sub> CH <sub>3</sub>		
15	3,4-dichlorophenyl	-chch_ch-	Н	н
		CH <sub>3</sub> CH <sub>3</sub>		
	3,5-dichlorophenyl	-CH-CH-	Н	Н
	C <sub>2</sub> H <sub>5</sub>	-CH2CH=CHCH2-	CH <sub>3</sub>	CH <sub>3</sub>
	2 7	CH <sub>3</sub> CH <sub>3</sub>	_	
20	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	-0404,04,04-	Н	CH <sub>3</sub>
	phenyl	-כוו, כוו=כווכוו,-	Н	Н
	phenyl	-c(cH <sub>3</sub> ) <sub>2</sub> cH=cHc(cH <sub>3</sub> ) <sub>2</sub> -	Н	Н
		CH <sub>3</sub> CH <sub>3</sub>		
	phenyl	-dhan_ch_ch-	Н	Н
25	phenyl	-c(cH <sub>3</sub> ) <sub>2</sub> cH <sub>2</sub> cH <sub>2</sub> c(cH <sub>3</sub> ) <sub>2</sub> -	Н	Н
	4-phenylphenyl	-CH2CH=CHCH2-	Н	Н
•		CH <sub>3</sub> CH <sub>3</sub>		
	4-phenylphenyl	-CH2C==CCH2-	Н	Н
	4-fluorophenyl	-CH2-CH=CHCH2-	Н	Н
30	4-chlorophenyl	-CH2CH2CH2CH2-	Н	Н
		n-C <sub>4</sub> H <sub>9</sub>		
	4-phenoxyphenyl	-CH2CH2CH2CH-	CH <sub>3</sub>	CH <sub>3</sub>
		CH <sub>3</sub> CH <sub>3</sub>		
	3-trifluoromethylphenyl	-CHCH=CHCH-	Н	CH <sub>3</sub>
35		CH <sub>3</sub> CH <sub>3</sub>		
	2-methoxyphenyl	-CH2CH-CHCH2-	н	Н

Preparation of (1,1'-Biphenyl-4-yl)dimethyl(lH-imida-zol-1-ylmethyl)silane

A mixture of 2.6 g (0.010 mol) of (1,1'-biphenyl-5 4-yl)chloromethyldimethylsilane and 1.1 g (0.012 mol) of imidazole sodium salt in 5 ml of dimethylformamide was warmed to 80-90° for 2 hours, cooled, diluted with water, and extracted with ether. The ether solution was washed with water and brine, dried over magnesium sulfate, and evaporated to leave 2.0 g of a viscous, pale yellow oil. Trituration of a small sample with hexanes gave a solid. The bulk of the crude product was then taken up in a hot mixture of 20 ml of hexanes and 3 ml of ethyl acetate, the solution was cooled slowly, and seed crystals were added when cloudiness was observed. The resulting crystals were collected and dried to give 0.84 g (29%) of the title compound as colorless flakes: m.p. 51-53°; ir (Nujol<sup>R</sup>) 1235, 1215, 1105, 1065, 900, 830, 785, 750, 730, 685 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.4 (6H, s), 3.7 (2H, s), 6.7 (1H, broad s), 7.0 (1H, broad s), 7.1-7.8 (10H, m); analysis for  $C_{18}H_{20}N_2Si$  (mw 292.45):

Calculated C, 73.92; H, 6.89; N, 9.58;

Found C, 73.4; H, 7.0; N, 9.4;

73.7; 7.0; 9.4.

30

Preparation of (4-Chlorophenyl)dimethyl(lH-imidazol--l-ylmethyl)silane

A mixture of 2.2 g (0.010 mol) of chloromethyl(4
5 chlorophenyl)dimethylsilane and 1.1 g (0.012 mol) of imidazole sodium salt in 5 ml of dimethylformamide was stirred at 80-90° for 2 hours, cooled, diluted with water, and extracted with ether. The ether solution was washed with water and brine, dried over magnesium sulfate, and evaporated to leave 2.0 g (81%) of the title compound as a yellow liquid: n<sub>0</sub><sup>20</sup> 1.5472; ir (neat) 1560, 1495, 1480, 1375, 1250, 1105, 1080, 905, 830, 810, 740 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.3 (6H, s), 3.6 (2H, s), 6.6 (1H, broad s), 6.9 (1H, broad s), 7.1 (1H, broad s), 7.3 (4H, s).

## Example 39

Preparation of (2,4-Dichlorophenyl)dimethyl(lHimidazol-l-ylmethyl)silane

20 A mixture of 5.1 g (0.020 mol) of chloromethyl(2,4-dichlorophenyl)dimethylsilane and 2.0 g (0.022
mol) of imidazole sodium salt in 10 ml of dry dimethylformamide was stirred at 80-90° for 2 hours and
worked up as in Example 18 to give 3.9 g (69%) of the
25 title compound as a brown oil: n<sub>0</sub><sup>23</sup> 1.5637; ir
(neat) 1560, 1500, 1450, 1355, 1250, 1105, 1095, 1075,
1025, 840, 780, 735 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.4 (6H, s),
3.9 (2H, s), 6.7 (1H, broad s), 7.0 (1H, broad s)
7.2-7.5 (4H, m).

Preparation of Diphenyl(lH-imidazol-l-ylmethyl)methylsilane

A mixture of 4.9 g (0.020 mol) of chloromethyl- (diphenyl)methylsilane and 2.0 g (0.022 mol) of imidazole sodium salt in 10 ml of dry dimethylformamide was stirred at 80°C for 3.5 hours and worked up as in Example 18 to give 4.8 g of a yellow oil. Kugelrohr distillation at 125°/0.05 mm removed volatile impurities, leaving behind 2.9 g (52%) of the title compound as an oil:  $n_D^{22}$  1.5995; ir (neat) 3375, 3250, 1500, 1430, 1255, 1230, 1110, 1075, 1025, 810, 790, 735, 700, 660 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) 0.6 (3H, s), 3.9 (2H, s), 6.6 (1H, broad s), 6.9 (1H, broad s), 7.2-7.5 (11H, m).

By applying the procedures of Example 37-40 to appropriate chloromethylsilanes, the compounds of Table XIV can be prepared.

20

25

30

, ز

# Table XIV

	R <u>i</u>	R <sub>2</sub>	R <sub>3</sub>	
10	CH <sub>3</sub>	CH <sub>3</sub>	СН <sub>3</sub>	$n_0^{22}$ 1.4805
	C <sub>2</sub> H <sub>5</sub> <u>i</u> -C <sub>3</sub> H <sub>7</sub>	сн <sub>3</sub>	_	n <sub>D</sub> <sup>22</sup> 1.4848
	<u>n</u> -C <sub>4</sub> H <sub>9</sub> <u>t</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>		n <sub>D</sub> 1.4811
15	<u>n</u> -C <sub>12</sub> H <sub>25</sub> <u>n</u> -C <sub>14</sub> H <sub>29</sub>	CH <sub>3</sub>	_	n <sub>D</sub> <sup>23</sup> 1.4585
	<u>n</u> -C <sub>18</sub> H <sub>37</sub> cyclopropyl	CH <sub>3</sub>		n <sub>D</sub> <sup>21</sup> 1.4639
20	cyclobutyl cyclopentyl	CH <sub>3</sub>	•	
	cyclohexyl	СН3	CH <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.4999
25	l-naphthyl 2-naphthyl	CH <sub>3</sub>	CH <sub>3</sub>	n <sub>0</sub> <sup>23</sup> 1.6188
	pheny1			bp 120-125° (0.05 mm)
	4-bromophenyl .	CH3.	CH <sub>3</sub>	n <sub>D</sub> <sup>20</sup> 1.5741
•	4-fluorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	n <sub>D</sub> <sup>23</sup> 1.5314
30	4-methoxyphenyl	CH <sub>3</sub>	CH <sub>3</sub>	n <sub>D</sub> <sup>25</sup> 1.5485
	4-phenoxyphenyl	CH <sub>3</sub>	CH <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.5833
	4-(4-chlorophenoxy)phenyl	CH <sub>3</sub>	CH <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.5564
	4-(4-fluorophenoxy)phenyl	CH <sub>3</sub>	CH <sub>3</sub>	
35	4-(4-trifluoromethylphenoxy)phenyl 4-(4-methylphenoxy)phenyl	CH <sub>3</sub>	•	

Table	VIV	(continued)

	R1	R <sub>2</sub>	R <sub>3</sub>	
	4-thiomethylphenyl	CH <sub>.3</sub>	CH <sub>3</sub>	$n_0^{23}$ 1.5855
5	4-methylsulfonylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	$n_{\rm D}^{21}$ 1.5552
	4-trifluoromethylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	$n_{\rm D}^{22}$ 1.4867
	4-methylphenyl	СН3	CH <sub>3</sub>	$n_{D}^{21}$ 1.5482
	4- <u>i</u> -propylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	<b>^</b>
10	4- <u>t</u> -butylphenyl	сн <sub>3</sub>	CH <sub>3</sub>	$n_0^{23}$ 1.5229
	4-cyclohexylphenyl	сн <sub>3</sub> -	CH <sub>3</sub>	n <sub>0</sub> <sup>22</sup> 1.5085
	4-trifluoromethoxyphenyl	CH3 .	CH <sub>3</sub>	$n_0^{22}$ 1.4888
	4-(4-chlorophenyl)phenyl	CH <sub>3</sub>	CH <sub>3</sub>	
15	4-(4-methylphenyl)phenyl	CH <sub>3</sub>	CH <sub>3</sub>	•
	4-(4-trifluoromethylphenyl)phenyl	CH <sub>3</sub>	CH <sub>3</sub>	
	4-(4-fluorophenyl)phenyl	CH <sub>3</sub>	CH <sub>3</sub>	
	4-(4-bromophenyl)phenyl	сн <sub>3</sub>	CH <sub>3</sub>	$n_0^{22}$ 1.5745
	3-phenylphenyl	сн <sub>3</sub>	CH <sub>3</sub>	n <mark>21</mark> 1.6002
20	3-trifluoromethylphenyl	ан <sub>3</sub>	CH <sub>3</sub>	$n_0^{20}$ 1.4927
	3-chlorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	$n_{\rm D}^{22}$ 1.5560
	2-trifluoromethylphenyl	CH <sub>3</sub>	СH <sub>3</sub>	nD 1.5056
25	2-phenylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.5996
	2-chlorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	nD 1.5382
	2-methoxyphenyl	сн <sub>3</sub>	CH <sub>3</sub>	$n_0^{22}$ 1.5344
	2,3—dimethylphenyl	CH <sub>3</sub>	CH <sub>3</sub>	•
30	2,3-dimethoxyphenyl	CH <sub>3</sub>	CH <sub>3</sub>	$n_{\rm D}^{22}$ 1.5350
	2,4-difluorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	
	2-fluoro-4-chlorophenyl	CHŹ	CH-	
	2-chloro-4-fluorophenyl	CH <sup>-2</sup>	ଫର୍	
	2-chloro-4-phenylphenyl	CH	CH <sub>3</sub>	
	3- "Horo-4-phenylohenyl		<b>~</b> .	
35	2-methyl-5-chlorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	

# Table XIV (continued)

	R1	R <sub>2</sub>	R <sub>3</sub>	
5	2,6-dimethoxyphenyl 2,6-dimethylphenyl	СН <sub>3</sub>	сн <sub>3</sub>	n <sub>D</sub> <sup>23</sup> 1.5348
	<ul><li>3,4-dichlorophenyl</li><li>3-methyl-4-fluorophenyl</li></ul>	CH <sub>3</sub>	сн <sub>3</sub>	n <sub>D</sub> <sup>23</sup> 1.5673
10	3,5-dichlorophenyl C <sub>2</sub> H <sub>5</sub> <u>i</u> -C <sub>3</sub> H <sub>7</sub>	C <sub>2</sub> H <sub>5</sub> cyclohexyl	сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.5461
	<u>n</u> -C <sub>4</sub> H <sub>9</sub> <u>n</u> -C <sub>10</sub> H <sub>21</sub> <u>n</u> -C <sub>12</sub> H <sub>25</sub> <u>n</u> -C <sub>14</sub> H <sub>29</sub>	n-C <sub>4</sub> H <sub>9</sub> cyclopropyl n-C <sub>3</sub> H <sub>7</sub> i-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.4710
20	n-C <sub>18</sub> H <sub>37</sub> cyclopropyl cyclopentyl cyclohexyl	3-methylbutyl n-C <sub>6</sub> H <sub>13</sub> cylopentyl cyclohexyl	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	
	l-naphthyl l-naphthyl 2-naphthyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub> <u>t</u> -C <sub>4</sub> H <sub>9</sub> n-C <sub>5</sub> H <sub>11</sub>	CH <sub>3</sub> CH <sub>3</sub>	
25	phenyl phenyl phenyl	n-C <sub>3</sub> H <sub>7</sub> n-C <sub>4</sub> H <sub>9</sub> 1,1-dimethylpropyl	сн <sub>3</sub> сн <sub>3</sub> сн <sub>3</sub>	n <sub>0</sub> <sup>22</sup> 1.5449
	phenyl 4-phenylphenyl 4-phenylphenyl 4-bromophenyl	<u>n</u> -C <sub>6</sub> H <sub>13</sub> C <sub>2</sub> H <sub>5</sub> <u>r</u> -C <sub>4</sub> H <sub>9</sub> <u>i</u> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	n <sub>D</sub> <sup>22</sup> 1.5880
30	4-chlorophenyl 4-fluorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub> <u>n</u> -C <sub>4</sub> H <sub>9</sub>	сн <sub>3</sub>	$n_{\rm D}^{21}$ 1.5415 $n_{\rm D}^{22}$ 1.5161
	4-phenoxyphenyl 4- <u>i</u> -propylphenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub> cyclopropyl	сн <sub>3</sub>	Ü
35	4- <u>t</u> -butylphenyl	<u>i</u> -c <sub>4</sub> H <sub>9</sub>	CH3	

Table XIV (continued)

	Ri	R <sub>2</sub>	R <sub>3</sub>	•
	3-phenylphenyl	i-CaH9	CH <sub>3</sub>	
5	3-trifluoromethylphenyl	S-CAH9	сн <sub>3</sub>	
	3-chlorophenyl	<u>n-C5H11</u>	CH <sub>3</sub>	
	2-methoxyphenyl	t-CaH9	CH <sub>3</sub>	
	2-thiomethylphenyl	cyclobutyl	CH <sub>3</sub>	
	2-phenylphenyl	<u>i</u> -C4H9	CH <sub>3</sub>	01
10	2,4-dichlorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	$n_0^{21}$ 1.5588
	2,4-dichlorophenyl	cyclopropyl	CH <sub>3</sub>	
	2,3-dimethylphenyl	<u>n</u> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	
	2-methyl-5-fluorophenyl	cyclopentyl	CH <sub>3</sub>	. **
	2,5-dimethoxyphenyl	4-methylpentyl	CH <sub>3</sub>	-
15	2,6-dimethylphenyl	l-methylbutyl	CH <sub>3</sub>	
	3,4-dichlorophenyl	<u>n</u> -C <sub>5</sub> H <sub>11</sub> '	CH <sub>3</sub>	
	3,5-dichlorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub> .	
	3,5-dichlorophenyl	cyclohexyl	CH <sub>3</sub>	
	3-methyl-4-chlorophenyl	cyclopropyl	CH <sub>3</sub>	10
20	4-fluorophenyl	phenyl	СН3	nD 1.5810
	4-chlorophenyl	phenyl	CH <sub>3</sub>	nD 1.6000
	4-bramophenyl	phenyl	CH <sub>3</sub>	$n_{\rm D}^{22}$ 1.6115
	4-phenylphenyl	phenyl	CH <sub>3</sub>	n <sub>D</sub> 1.6378
25	4-t-butylphenyl	phenyl	CH <sub>3</sub>	
	4-thiomethylphenyl	phenyl	CH <sub>3</sub>	
	4-phenoxyphenyl	phenyl	CH <sub>3</sub>	•
	4-trifluoromethoxyphenyl	phenyl	CH <sub>3</sub>	
30	4-methylsulfonylphenyl	phenyl	CH <sub>3</sub>	
	4-cyclahexylphenyl	phenyl	CH <sub>3</sub>	
	4-(4-fluorophenyl)phenyl	phenyl	CH <sub>3</sub>	
	3-trifluoromethylphenyl	phenyl	CH <sub>3</sub>	
	2-chlorophenyl	phenyl	Сн <sup>и</sup>	-22 1 1050
٠.	e in sittingerit	aheny:		

# Table XIV (continued)

	$\frac{R_1^i}{2}$ .	<u>R2</u>	R <sub>3</sub>		
5	2,4-dichlorophenyl	phenyl	CH <sub>-2</sub>	n <sub>D</sub> 22	1.6150
)	2-chloro-4-phenylphenyl	phenyl	CH <sub>3</sub>	ט	
	2-fluoro-4-phenylphenyl	phenyl	CH <sub>3</sub>		
	3,5-dichlorophenyl	phenyl	CH <sub>3</sub>		
	2,5-dimethoxyphenyl	pheny1	СН <sub>3</sub>		•
10	2,6-dimethoxyphenyl	phenyl	CH <sub>3</sub>		
10	4-fluorophenyl	4-fluorophenyl	CH <sub>3</sub>	n <sub>D</sub> 22	1.5569
	4-chlorophenyl	4-chlorophenyl	CH <sub>3</sub>	O	1.5820
	4-bromophenyl	4-bromophenyl	CH <sub>3</sub>	n21	1.6305
	4-phenylphenyl	4-phenylphenyl	CH <sub>3</sub>	m.p.	. 44 <del>-</del> 53°
15	4-methoxyphenyl	4-methoxyphenyl	CH <sub>3</sub>	21	1.5947
•	3-trifluoromethylphenyl	3-trifluoromethylphenyl	_	U	
	2-chlorophenyl	2-chlorophenyl	CH <sub>3</sub>	n <sub>D</sub> 20	1.5999
	2-methoxyphenyl	2-methoxyphenyl	CH <sub>3</sub>	00	
20	2,4-dichlorophenyl	2,4-dichlorophenyl		n <sub>D</sub> 22	1.6019
	3,5-dichlorophenyl	3,5-dichlorophenyl	CH <sub>3</sub>		
	2-chlorophenyl	4-chlorophenyl	CH <sub>3</sub>	n <sub>D</sub> 20	1.6044
	2-chlorophenyl	4-fluorophenyl	CH <sub>3</sub>		
	4-phenylphenyl	4-chlorophenyl	CH3.		•
25	4-phenylphenyl	4-fluorophenyl	CH <sub>3</sub>		
	4-phenylphenyl	2,4-dichlorophenyl	CH <sub>3</sub>		
	4-fluorophenyl	2,4-dichlorophenyl	CH <sub>3</sub>		
	4-chlorophenyl	2,4-dichlorophenyl	CH <sub>3</sub>		
	1-naphthy1	2,6-dimethoxyphenyl	CH <sub>3</sub>		
30	4-phenoxyphenyl	3,4-dichlorophenyl	сн <sub>3</sub>		
	<sup>C</sup> 2 <sup>H</sup> 5	<sup>C</sup> 2 <sup>H</sup> 5	C <sub>2</sub> H <sub>5</sub>		
	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	<u>i</u> -c <sub>3</sub> 1	-	
	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	n-C4	-	_
	<u>n</u> -C <sub>8</sub> H <sub>17</sub>	C <sub>2</sub> H <sub>5</sub>	cyclo		
35	<u>n</u> -C <sub>14</sub> H <sub>29</sub>	cyclopropyl	1-me	thyli	outyl

## Table XIV (continued)

	R1	R <sub>2</sub> .	<u>R</u> 3
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	<u>n</u> -C <sub>6</sub> H <sub>13</sub>	n-C6H13
5	cyclopropyl	C <sub>2</sub> H <sub>5</sub>	s-C4H9
	cyclohexyl .	<u>п</u> -С <sub>3</sub> Н <sub>7</sub>	<u>n</u> -C <sub>3</sub> H <sub>7</sub>
	l-naphthyl	n-C4H9	n-C4H9
	2-naphthy1	n-C <sub>4</sub> H <sub>9</sub>	cyclobutyl
•	phenyl .	cyclopropyl	<u>n-</u> C6H13
10	4-phenylphenyl	С <sub>2</sub> Н <sub>5</sub>	с <sub>2</sub> н <sub>5</sub>
	4-phenylphenyl	n-C4H9	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
	4-phenylphenyl	<u>п</u> -с <sub>е</sub> нз	<u>n-</u> C6H <sub>13</sub>
	4-phenylphenyl	cyclohexyl	cyclohexyl
	4-chlorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
15	4-fluorophenyl	<u>r</u> –C <sub>3</sub> H <sub>7</sub>	<u>n</u> -c <sub>3</sub> H <sub>7</sub>
	4-phenoxyphenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	cyclohexyl
	4-(4-chlorophenoxy)phenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
	4 <u>t</u> -butylphenyl	<u>s</u> -C <sub>4</sub> H <sub>9</sub>	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
	3-methoxyphenyl	с <sub>2</sub> н <sub>5</sub>	<u>t</u> -C <sub>4</sub> H <sub>9</sub>
20	3-trifluoromethylphenyl	<u>s</u> -C <sub>4</sub> H <sub>9</sub>	s-C <sup>E</sup> H <sub>3</sub>
	2-thiomethylphenyl	<u>i-</u> C <sub>3</sub> H <sub>7</sub>	3-methylbuty.
	2-phenylphenyl	cyclohexyl	cyclohexyl
	2,4-dichlorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>n</u> -C <sub>4</sub> H <sub>9</sub>
	2,6-dimethylphenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	<u>t</u> -C <sub>4</sub> H <sub>9</sub>
25	3,5—dichlorophenyl	cyclopentyl	cyciopentyl
	3-methyl-4-chlorophenyl	<u>s</u> -C <sub>4</sub> H <sub>9</sub>	s-C4H9
	2-methyl-5-fluorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
	с <sub>2</sub> н <sub>5</sub>	phenyl	phenyl
	cyclohexyl	phenyl	phenyl
30	<u>n</u> –C <sub>18</sub> H <sub>37</sub>	phenyl	phenyl
	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	4-chlorophenyl	4-chlorophenyl
	<u>n-C<sub>12</sub>H<sub>25</sub></u>	4-chlorophenyl	4-chlorophenyl
	l-naphthyl	4-fluoronhenvl	4-fluoropheryl
-	TV/ Harring VI	pher-	Samabagy (nprm)
;	<u>n-0,</u> dg	pnen-	<u>ของกรค</u> องไปที่คาง ,

Table XIV (continued)

			-
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	phenyl .	2,4-dichlorophenyl
5	<u>n</u> -C <sub>3</sub> H <sub>7</sub>	phenyl	3-trifluoromethylphenyl
	i-CAH,	phenyl	3,5-dichlorophenyl
	cyclopentyl	phenyl	2,6-dimethoxyphenyl
	n-C <sub>14</sub> H <sub>29</sub>	4-chlorophenyl	2-fluorophenyl
	<u>n</u> -C <sub>A</sub> H <sub>9</sub>	4-fluorophenyl	4-phenylphenyl
10	phenyl	phenyl	phenyl m.p. 175-178°
	4-chlorophenyl	4-chlorophenyl	4-chlorophenyl
	4-fluorophenyl	4—fluorophenyl	4-fluorophenyl
	4-phenylphenyl	4-phenylphenyl	4-phenylphenyl
•	2,4-dichlorophenyl	2,4-dichlorophenyl	2,4-dichlorophenyl
15	phenyl	4-fluorophenyl	4-fluorophenyl
	phenyl	4-chlorophenyl	4-chlorophenyl
	phenyl	4-phenylphenyl	4-phenylphenyl
	phenyl	2,4-dichlorophenyl	2,4-dichlorophenyl
	2-naphthyl	4-methylthiophenyl	4-methylthiophenyl
20	4-chlorophenyl	2-methoxyphenyl	2-methoxyphenyl
	4-chlorophenyl	3-chlorophenyl	3-chlorophenyl .
	phenyl	2-chlorophenyl	4-fluorophenyl
	phenyl	4-chlorophenyl	4-phenylphenyl
	l-naphthyl	4-bromophenyl	3-methylphenyl
25	4-phenoxyphenyl	3,5-dimethylphenyl	3,4-dichlorophenyl

## Example 41

Preparation of (1,1'-Biphenyl-4-yl)dimethyl(2-methyllH-imidazol-1-ylmethyl)silane

The title compound is prepared by applying the procedure of Example 37 to (1,1'-biphenyl-4-yl)chloromethyldimethylsilane and the sodium salt of 2-methyl-imidazole.

Related compounds may be made in this way using salts of 2,4-dimethylimidazole, 4,5-dimethylimidazole, 10 and 2,4,5-trimethylimidazole.

The procedure of Example 41 may be used to prepare the compounds of Table XV.

15

20

25

- الأنجار و المار ال

10 n-C18H37 cyclohexyl CH3  $CH_{\prec}$ 1-naphthyl CH3 CH<sub>3</sub> CHZ phenyl 15 CH<sub>3</sub> phenyl CH<sub>3</sub> Н Н CH3 4-phenylphenyl Н Н Н CH Н 4-(4-fluorophenyl)phenyl CH3 4-phenoxyphenyl CH3 3-trifluoromethylphenyl CHZ 20 СHĻ 2-methoxyphenyl CH3 2,4-dichlorophenyl CH3 CHZ CHZ 2-chloro-4-phenylphenyl CH CH<sub>3</sub> pheny1 U-CVH2 CH CH Н CH<sub>3</sub> 4-phenylphenyl n-C4H9 Н CH 25 CH<sub>3</sub> n-C6H13 2,4-dichlorophenyl CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> 4-(4-chlorophenoxy)phenyl Н cyclohexyl CH<sub>3</sub> CH<sub>3</sub> phenyl pheny1 CH<sub>3</sub> 4-fluorophenyl pheny l CH-CH3 4-fluorophenyl phenyl 30 4-chlorophenyl phenyl CH CH-CH 4-fluorophenyl 4-fluorophenyl CH, H٠ CHZ 4-fluorophenyl 4-fluorophenyl 4-chlorophenyl ----incopnenyi

a-rhiotoorery.

93
Table XV (continued)

	R <u>i</u>	R <sub>2</sub>	<u>R</u> 3	$\frac{q_1}{2}$	<u>Q</u> 2	<u>Q</u> 3
5	2-chlorophenyl	4-chlorophenyl	대국	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	2,4-dichlorophenyl	2,4-dichlorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	Н	Н
	n-C <sub>18</sub> H <sub>37</sub>	n-c <sub>6</sub> H <sub>13</sub>	n-C6H13	Н	CH <sub>3</sub>	CH3
	1-naphthy1	n-C4H9	n-C4H9	CH	CH <sub>3</sub>	CH <sub>3</sub>
	phenyl.	pheny1	phenyl.	CH <sub>3</sub>	Н	н
10	phenyl	phenyl	pheny1	CH <sub>3</sub>	Н	CH <sub>3</sub>
	phenyl	phenyl	phenyl	CH <sub>3</sub>	CH3	Н

Preparation of the 1:1 complex of (1,1'-8iphenyl-4-yl)-dimethyl(lH-imidazol-1-ylmethyl)silane and Cuprous Chloride

A mixture of 0.50 g (0.0017 mol) of (1,1'-bi-phenyl-4-yl)dimethyl(lH-imidazol-1-ylmethyl)silane and 0.22 g (0.0017 mol) of cuprous chloride in 15 ml of tetrahydrofuran was refluxed under N<sub>2</sub> for 15 minutes, and the resulting deep green solution was evaporated to leave the title complex as a dark green solid: m.p. 72-80° (decomp.); ir (Nujol<sup>R</sup>) 1590, 1515, 1250, 1110, 840, 820, 750, 695, 650 cm<sup>-1</sup>.

By applying the procedure of Example 24, any of the compounds of Tables XIV, XV, XVI, XVII, XVIII or 15 XIX can be converted to metal complexes or salts.

#### Example 43

Preparation of (1,1-'Biphenyl-4-yl)(1H-imidazol-1-ylmethyl)(methoxy)methylsilane

A mixture of (1,1'-biphenyl-4-yl)chloro(chloromethyl)methylsilane and two equivalents of imidazole
sodium salt in dimethylformamide is warmed to 80-90°C
for 2 hours. Ten equivalents of methanol is then
added, and the mixture is held at 70° for 1 hour,
25 cooled, diluted with water, and quickly extracted with
ether. Washing the ether solution with water and
brine, drying over magnesium sulfate, and evaporation
leaves the title compound.

Related compounds can be made in the same way, using the appropriate chlorosilane and alcohol; for  $R_6 = OH$ , water is used instead of an alcohol, and hydrolysis is conducted at 20-25° instead of 70°.

Preparation of 1,1-(Dimethylethoxy)(1H-imidazol-1-y1-methyl)methyl(phenyl)silane

A mixture of 3.6 g (0.015 mol) of chloromethyl-5 (1,1-dimethylethoxy)methyl(phenyl)silane and 1.3 g (0.015 mol) of imidazole sodium salt in 10 ml of dimethylformamide was stirred at 50° for 3 hours, allowed to stand at room temperature for 72 hours, poured into water, and extracted with ether. The 10 ether extracts were washed three times with water and once with brine, dried over magnesium sulfate, and evaporated to leave 3.8 g of an oil. Impurities were removed by Kugelrohr distillation at 90° (airbath)/ 0.05 mm to leave 2.9 g (71%) of the title compound as a pale yellow oil:  $n_n^{20}$  1.5291; ir (neat) 3105, 3070, 3045, 2970, 1590, 1500, 1425, 1360, 1250, 1235, 1185, 1110; 1055, 1020, 900, 805, 740, 700, 660 cm<sup>-1</sup>; nmr  $(CDCl_3): 0.6 (3H, s), 1.3 (9H, s), 3.6 (2H, s), 6.8$ (1H, s), 7.0 (1H, s) and 7.3-7.7 (6H, m).

The compounds of Tables XVI and XVII can be made using the procedures of Examples 43 and 44.

25

20

## Table XVI

Ri-si-CH2N N

5

CH<sub>3</sub> t-C4H9 10 CH<sub>3</sub> C2H5 CH<sub>3</sub> C2H5 CH<sub>3</sub> n-C6H13 n-C<sub>18</sub>H<sub>37</sub> S-C4H9 CH<sub>3</sub> cyclopropyl CH<sub>3</sub> CH<sub>3</sub> cyclohexyl 15 i-C3H7 1-C3H7 1-naphthyl cyclobutyl <u>п</u>-С<sub>3</sub>H<sub>7</sub> 2-naphthy1 CH<sub>3</sub> phenyl CH<sub>3</sub> CH<sub>3</sub>. pheny1 CH<sub>3</sub> C2H5 phenyl 20 CH<sub>3</sub> i-C3H7 pheny1 t-C4H9 phenyl CH<sub>3</sub> 4-phenylphenyl <u>r-</u>C4H9 t-CAH9 Н 4-phenylphenyl C2H5 CH<sub>3</sub> 4-phenylphenyl 25 CH3 n-CAH9 4-phenylphenyl n-CAH9 n-CAH9 4-chlorophenyl CH<sub>3</sub> CH<sub>3</sub> 4-chlorophenyl CH<sub>3</sub> C2H5 4-chlorophenyl n-C-Hn-C6H13 4-fluorophenyl 30 CH<sub>3</sub> C2H5 4-fluorophenyl cyclohexyl i-C4H9 4-phenoxyphenyl 4-t-butylphenyl n-C3H7 . S-C4H9 3-trifluoromethylphenyl t-CAH9 Н 2-methylthiophenyl C2H= cyclopentyl 35

# Table XVI (continued)

	•		
	R!	<del>R2</del>	R <sub>6</sub>
	2,4-dichlorophenyl	CH <sub>3</sub>	CH <sub>3</sub>
5	2,4-dichlorophenyl	сн <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> .
	2,4-dichlorophenyl	CH <sub>3</sub>	t-C4H9
	2,4-dichlorophenyl	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	C <sub>2</sub> H <sub>5</sub>
	2,3-dimethylphenyl	cyclopropyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>
	2-methyl-5-fluorophenyl	s-CAHo	n-C <sub>3</sub> H <sub>7</sub>
10	2,6-dimethoxyphenyl	l,l-dimethylpropyl	— ) / Н
	3-methyl-4-chlorophenyl	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>
	3,5-dichlorophenyl	<u>n</u> -C <sub>5</sub> H <sub>11</sub>	C <sub>2</sub> H <sub>5</sub>
	<u>n-C<sub>12</sub>H<sub>25</sub> .</u>	2,4-dichlorophenyl	t-CaH9
	n-C <sub>18</sub> H <sub>37</sub>	phenyl	CH <sub>3</sub>
15	l-naphthyl	phenyl	C <sub>2</sub> H <sub>5</sub>
	pheny1	phenyl	t-C4H9
	4-fluorophenyl	phenyl	CH <sub>3</sub>
	4-chlorophenyl	phenyl	<u>n-C</u> 3H7
	4-phenylphenyl	phenyl	C2H5
20	4-phenylphenyl	phenyl	S-C4H9
	4-t-butylphenyl	phenyl ·	S-C4H9
	3-fluorophenyl	pheny1	C2H5
	2-methoxyphenyl	phenyl	Н
٥.	2-chlorophenyl	phenyl	CH <sub>3</sub>
25	2,4-dichlorophenyl	phenyl .	<u>i-</u> C <sub>3</sub> H <sub>7</sub>
	3,5-dichlorophenyl	phenyl	<u>n</u> -C <sub>3</sub> H <sub>7</sub>
	4-fluorophenyl	4-fluorophenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub>
	4-fluorophenyl	4-fluorophenyl	C2H5
30	4-chlorophenyl	4-chlorophenyl	CH <sub>3</sub>
<b>J</b> U	4-chlorophenyl	4-chlorophenyl	C <sub>2</sub> H <sub>5</sub>
	4-phenylphenyl	4-phenylphenyl	CH <sub>3</sub>
	2,4-dichlorophenyl	2,4-dichlorophenyl	C2H5
	3-trifluoromethylphenyl	3-trifluoromethylphenyl	<u>i</u> -C <sub>4</sub> H <sub>9</sub>
75	2-methoxyphenyl	2-methoxyphenyl	Н
35	2-chlorophenyl	4-fluorophenyl	Н

# 98 Table XVI (continued)

	Ri	R <sub>2</sub>	<sup>R</sup> 6
	3-trifluoromethylphenyl	4-t-butylphenyl	n-C4H9
5	2-fluoro-4-chlorophenyl	4-bromophenyl	i-C3H7
	2,3-dimethylphenyl	4-methylthiophenyl	C2H5
	2,6-dimethoxyphenyl	4-methoxyphenyl	Н
	3,4-dichlorophenyl	4-methylphenyl	<u>i</u> -C4H9

# Table XVII

	Ri	<u>R</u> 2	R <sub>6</sub>	$\frac{Q_1}{Q_1}$	$\frac{Q_2}{2}$	Q <sub>3</sub>
10	C-H5	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
10	cyclohexyl	CH <sub>3</sub>	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	н	CH <sub>3</sub>	CH <sub>3</sub>
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	<u>n</u> -c <sub>6</sub> H <sub>13</sub> ·	t-CAH9	CH-3	н	н
	1-naphthy1	CH <sub>3</sub>	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	CH3	Н	Н
	phenyl	CH <sub>3</sub>	t-C4H9	н	CH <sub>3</sub>	Н
15	phenyl	CH <sub>3</sub>	t-C4H9	Н	н	CH <sub>3</sub>
17	phenyl	CH <sub>3</sub>	t-C4H9	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	phenyl	CH <sub>3</sub>	s-C4H9	Н	CH <sub>3</sub>	CH <sub>3</sub>
	phenyl	CH <sub>3</sub>	<u>i</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	·H	Н
	4-phenylphenyl	<u>n-</u> C <sub>4</sub> H <sub>9</sub>	t-C4H9	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
20	4-phenylphenyl	CH <sub>3</sub>	t-C4H9	CH <sub>3</sub>	н	н
20	4-phenylphenyl	CH <sub>3</sub>	t-C4H9	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	4-chlorophenyl	CH <sub>3</sub>	t-C4H9	CH <sub>3</sub>	Н	Н
	4-chlorophenyl	CH <sub>3</sub>	t-C4H9	Н	CH <sub>3</sub>	CH <sub>3</sub>
	4-fluorophenyl	CH <sub>3</sub>	t-C4H9	Н	CH <sub>3</sub>	Н
25	4-fluorophenyl	CH <sub>3</sub>	t-C4H9	Н	Н	CH <sub>3</sub>
-	phenyl	phenyl .	C2H5	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	phenyl	phenyl	п-С <sub>3</sub> Н7	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	4-fluorophenyl	phenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	Н	CH <sub>3</sub>	CH <sub>3</sub>
	4-fluorophenyl	phenyl	t-C4H9	CH <sub>3</sub>	Н	Н
30	4-chlorophenyl	phenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	Н	Н
	2,4-dichlorophenyl	phenyl	Н	CH <sub>3</sub>	Н	Н
	4-fluorophenyl	4-fluorophenyl	t-C4H.9	CH <sub>3</sub>	Н	H
	4-fluorophenyl	4-fluorophenyl	<u>t</u> -C4H9	Н	CH <sub>3</sub>	CH <sub>3</sub>
	4-fluorophenyl	4-fluorophenyl	<u>t</u> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
35	2-methoxyphenyl	2-methoxyphenyl	C2H5	CH <sub>3</sub>	Н	Н
	3-methylphenyl	3-methylphenyl	i-C4H9	CH <sub>3</sub>	Н	Н

## Example 45

Preparation of (lH-Imidazol-l-ylmethyl)phenylbis(2-propoxy)silane

The title compound can be made by applying the procedure of Example 26 to chloromethyl(phenyl)bis-(2-propoxy)silane:  $n_0^{22}$  1.4971; nmr (CDCl<sub>3</sub>) 1.2 (12H, d, J = 6), 3.6 (2H, s), 4.2 (2H, septet, J = 6), 6.8-7.6 (8H, m).

The compounds of Tables XVIII and XIX can be made similarly.

# 101 Table XVIII

OR6
Ri-si-cH2N
OR6

	Ri	R 6	$\frac{q_1}{}$	Q <sub>2</sub>	$Q_3$
10	с <sub>2</sub> н <sub>5</sub>	t-C4H9	н	Н	н
	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	C2H5	Н	Н	Н
	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	CH <sub>3</sub>	н	Н	н
	cyclohexyl	n-C3H7	Н	Н	Н
	l-naphthyl	i-C4H9	Н	Н	Н
15	phenyl	CH <sub>3</sub>	· CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	phenyl	n-C3H7	CH <sub>3</sub>	H .	Н
	phenyl	i-C3H7		CH <sub>3</sub>	CH <sub>3</sub>
•	phenyl	t-C4H9	н	Н	Н
	4-phenylphenyl	C2H5	H	Н	Н
20	4-phenylphenyl	n-C4H9	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	4-fluorophenyl	CH <sub>3</sub>	CH <sub>3</sub>	Н	Н
	4-fluorophenyl	C2H5	Н	Н	Н
	4-chlorophenyl	C <sub>2</sub> H <sub>5</sub>	Н	Н	н
	4-chlorophenyl	<u>i</u> -C <sub>3</sub> H <sub>7</sub>	Н	Н	Н
25	3-trifluoromethylphenyl	<u>s-C4H9</u>		CH <sub>3</sub>	CH3
	2-methoxyphenyl	n-C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	Н	H
	2,3-dimethylphenyl	1-C4H9	Н	Н	Н
	2,4-dichlorophenyl	CH <sub>3</sub>	Н	Н	н
7.0	2,4-dichlorophenyl	с <sub>2</sub> н <sub>5</sub>	· H	Н	Н
30	2-methoxy-5-fluorophenyl	<u>i-</u> C <sub>3</sub> H <sub>7</sub>	Н	Н	Н
	2,6-dimethoxyphenyl.	CH <sub>3</sub>	Н	н	Н
	3,4-dichlorophenyl	C <sub>2</sub> H <sub>5</sub>	Н	H	Н
	3,5-dichlorophenyl	n-C4H9	Н	Н	Н

# Table XIX

	Ri	R <sub>6</sub>	$\frac{\mathbf{Q}_1}{\mathbf{Q}_1}$	$Q_2$	Q <sub>3</sub>
10	C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> CH <sub>2</sub> -	н	Н	H .
	<u>n</u> -C <sub>4</sub> H <sub>9</sub>	сн <sub>3</sub> -сн <sub>2</sub> сн-	CH <sub>3</sub>	н	н
	n-C <sub>18</sub> H <sub>37</sub>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	Н	CH <sub>3</sub>	CH <sub>3</sub>
15	cyclahexyl	с <sub>2</sub> н <sub>5</sub> -сн <sub>2</sub> сн-	CH <sub>3</sub>	СН3	CH3
	l-naphthyl	-CH <sub>2</sub> CH <sub>2</sub> -	CH <sub>3</sub>	Н	Н
	phenyl	-CH <sub>2</sub> CH <sub>2</sub> -	Н	Н	Н
20	pheny1	C <sub>2</sub> H <sub>5</sub> -CH <sub>2</sub> CH- n-C-H-	Н	н	н
	phenyl	<u>п</u> -С <sub>3</sub> н <sub>7</sub> -Сн <sub>2</sub> Сн-	Н	Н	Н
	phenyl	-c(CH <sub>3</sub> ) <sub>2</sub> c(CH <sub>3</sub> ) <sub>2</sub> -	Н	Н	Н
	4-phenylphenyl	-CH <sub>2</sub> CH <sub>2</sub> -	н	Н	Н
25	4-phenylphenyl	C <sub>2</sub> H <sub>5</sub> -CH <sub>2</sub> CH-	н	Н	Н
	4-phenylphenyl	CHCH-	н	н	н
	4-fluorophenyl	-CH2CH2-	Н	н	Н
30	4-fluorophenyl	сн <sub>3</sub> -сн <sub>2</sub> сн-	н	н	н
	4-chlorophenyl	C <sub>2</sub> H <sub>5</sub> -CH <sub>2</sub> CH-	н	Н	н
	4-chlorophenyl	-C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> -	Н	Н	Н
35	3-trifluoromethylphenyl	CH <sub>3</sub> -CHCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> -	ᅄ	CH.,	CH-
		, , ,	,		,

# Table XIX (continued)

	R' <u>1</u>	R <sub>6</sub>	$\frac{q_1}{1}$	$\frac{Q_2}{2}$	<u>Q</u> 3
5	2 mathagushasul	<u>п</u> -С <sub>4</sub> Н <sub>9</sub> -СН <sub>2</sub> СН-	СН3	н	н
	2-methoxyphenyl	_	_		
	2,3-dimethylphenyl	-CH <sub>2</sub> CH <sub>2</sub> - C <sub>2</sub> H <sub>5</sub>	Н	CH <sub>3</sub>	CH <sub>3</sub>
	2,4-dichlorophenyl	-CH2CH-	Н	Н	Н
10	2,4-dichlorophenyl	<u>г</u> -С <sub>3</sub> H <sub>7</sub> -сн <sub>2</sub> сн-	Н	н	Н
		CH <sub>3</sub> CH <sub>3</sub>			
	2-methoxy-5-fluorophenyl	-ċнс(ан <sub>3</sub> ) <sub>2</sub> àн-	CH <sub>3</sub>	Н	Н
•	2,6-dimethoxyphenyl	-CH <sub>2</sub> CH <sub>2</sub> -	Н	Н	Н
		CH <sub>3</sub> CH <sub>3</sub>			
15	3,4-dichlorophenyl	- כיאכא-	CH3	CH <sub>3</sub>	CH
		CH <sub>3</sub> CH <sub>3</sub>			,
	3,5-dichlorophenyl	-CHCH-	CH <sub>-</sub>	CH <sub>3</sub>	CH-
	C <sub>2</sub> H <sub>5</sub>	-CH2CH=CHCH2-	H·	CH <sub>3</sub>	
•	2.5	CH <sub>3</sub> CH <sub>3</sub>		,	
20	<u>n</u> -C <sub>18</sub> H <sub>37</sub>	- באכא, בא, בא-	Н	CH <sub>3</sub>	CH-
	phenyl	-CH_CH=CHCH	Н	Н	Н
	phenyl	-c(cH <sub>3</sub> ) <sub>2</sub> cH=CHc(cH <sub>3</sub> ) <sub>2</sub> -	Н	н	н
	p.,,2	CH <sub>3</sub> CH <sub>3</sub>			
	pheny1	-כאכא, כא, כא-	Н	Н	Н
25	phenyl	-c(cH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> -	Н	Н	Н
	4-phenylphenyl	-CH2CH=CHCH2-	Н	Н	Н
		та сн <sub>3</sub>			
	4-phenylphenyl	-CH_C=CCH	н	Н	Н
	4-fluorophenyl	-CH2-CH=CHCH2-	Н	Н	Н
30	4-chlorophenyl	-CH2CH2CH2CH2-	Н	Н	Н
		<u>n</u> -c <sub>4</sub> H <sub>9</sub>			
	4-phenoxyphenyl	-CH_CH_CH_CH-	CH <sup>-</sup> 3	Н	Н
		CH <sub>3</sub> CH <sub>3</sub>			
	3-trifluoromethylphenyl	-CHCH=CHCH-	н	CH-	CH <sub>3</sub>
35	•	CH <sub>3</sub> CH <sub>3</sub>	•		
	2-methoxyphenyl	-CH2CH-CHCH2-	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>

## **Formulations**

Useful formulations of the compounds within the scope of this invention can be prepared in conventional ways. They include dusts, granules, pellets, solu-5 tions, emulsions, wettable powders, emulsifiable concentrates and the like. Many of these may be applied directly. Sprayable formulations can be extended in suitable media and used at spray volumes of from a few pints to several hundred gallons per acre. High 10 strength compositions are primarily used as intermediates for further formulations. The formulations. broadly, contain about 1% to 99% by weight of active ingredient(s) and at least one of a) about 0.1% to 20% surfactant(s) and b) about 5% to 99% solid or liquid 15 inert diluent(s). More specifically, they will contain these ingredients in the following approximate proportions:

	1 1 · · · · · · ·			
		Active	Percent	by Weight
20	·		Diluent(s)	Surfactant(s)
	Wettable Powders	20-90	0-74	1-10
	Oil Suspensions, Emulsions, Solutions, (including Emulsifiab Concentrates)	5 <b>-</b> 50 le	40-95	0-15
25	Aqueous Suspensions	10-50	40-84	1-20
	Dusts .	1-25	70-99	0-5
	Granules and Pellets	1-95	5 <b>-</b> 99	0-15
	High Strength Compositions	90-99	0-10	0-2

Jower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the compound. Higher ratios of surfactant to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

Typical solid diluents are described in Watkins, et al., "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Dorland Books, Caldwell, New Jersey. The more absorptive diluents are preferred 5 for the wettable powders and the denser ones for dusts. Typical liquid diluents and solvents are described in Marsden, "Solvents Guide," 2nd Ed., Interscience, New York, 1950. Solubility under 0.1% is preferred for suspension concentrates; solution 10 concentrates are preferably stable against phase separation at 0°C. "McCutcheon's Detergents and Emulsifiers Annual", MC Publishing Corp., Ridgewood, New Jersey, as well as Sisely and Wood, "Encyclopedia of Surface Active Agents", Chemical Publishing Co., 15 Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc.

The methods of making such compositions are well
known. Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer or fluid energy mill. Suspensions are prepared by wet milling (see, for example, Littler, U.S. Patent
3,060,084). Granules and pellets may be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See J. E. Browning, "Agglomeration", Chemical Engineering, December 4, 1967, pp. 147ff. and "Perry's Chemical Engineer's Handbook", 4th Ed., McGraw-Hill, New York, 1963, pp. 8-59ff.

### Example 46

	Evample 40	
	Wettable Powder	
	(1,1-Biphenyl-4-yl)dimethyl(1H-1,2,4-tri	azol-l-yl-
	methyl)silane	40%
5	dioctyl sodium sulfosuccinate	1.5%
	sodium ligninsulfonate	. 3%
	low viscosity methyl cellulose .	1.5%
	attapulgite	54%
	The ingredients are thoroughly ble	nded, pass
LO	through an air mill, to produce an avera	de darticl

The ingredients are thoroughly blended, passed

10 through an air mill, to produce an average particle

size under 15 microns, reblended, and sifted through a

U.S.S. No. 50 sieve (0.3 mm opening) before packaging.

All compounds of the invention may be formulated in the same manner.

15 Example 47

#### Wettable Powder

20

(4-8romophenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane 20%

sodium alkylnaphthalenesulfonate 2% low viscosity methyl cellulose 2%

diatomaceous earth 76%

The ingredients are blended, coarsely hammer-milled and then air milled to produce particles of active essentially all below 10 microns in diameter.

25 The product is reblended before packaging.

#### Example 48

#### High Strength Concentrate

(4-Chlorophenyl)dimethyl(lH-1,2,4-triazol-1-yl-methyl)silane 98.5%

30 silica aerogel 0.5%

synthetic amorphous fine silica 1.0%

The ingredients are blended and ground in a hammer-mill to produce a high strength concentrate essentially all passing a U.S.S. No. 50 sieve (0.3 mm openings). This material may then be formulated in a

variety of ways.

#### Example 49

UUST	D	u	s	t
------	---	---	---	---

5

high strength concentrate from

Example 48 25.4%

pyrophyllite, powdered 74.6%

The incredients are thoroughly blended and

The ingredients are thoroughly blended and packaged for use.

#### Example 50

#### Aqueous Suspension

10 (1,1'-Biphenyl-4-yl)dimethyl(1H-1,2,4-triazol-1-yl-50.0% methyl)silane 0.3% polyacrylic acid thickener dodecylphenyl polyethylene glycol 0.5% ether 15 1.0% disodium phosphate 0.5% monosodium phosphate polyvinyl alcohol 1.0% 0.4% pentachlorophenyl 46.3% water

The ingredients are ground together in a sand mill to produce particles substantially all under five microns in size.

#### Example 51

#### Emulsifiable Concentrate

25 Dimethyl(phenyl)(lH-1,2,4-triazol-1-ylmethyl)-

silane 20%

chlorobenzene 74%

sorbitan monostearate and poly-

oxyethylene condensates thereof. 6%

The ingredients are combined and stirred to produce a solution which can be emulsified in water for application.

#### Example 52

#### Emulsifiable Concentrate

Dimethyl(4-methylphenyl)(1H-1,2,4-triazol-1-ylmethyl)-silane 30%

5 blend of oil soluble sulfonates

and polyoxyethylene ethers 4%

xylene 66%

The ingredients are combined and stirred with gentle warming to speed solution. A fine screen 10 filter is included in packaging operation to insure the absence of any extraneous undissolved material in the product.

#### Example 53

#### Granule

15 wettable powder of example 46 15% gypsum 69% potassium sulfate 16%

The ingredients are blended in a rotating mixer and water sprayed on to accomplish granulation. When 20 most of the material has reached the desired range of 1.0 to 0.42 mm. (U.S.S. # 18 to 40 sieves), the granules are removed, dried, and screened. Oversize material is crushed to produce additional material in the desired range. These granules contain active ingredient.

#### Example 54

#### Emulsifiable Concentrate

(2,4-Dichlorophenyl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane 30%

30 blend of oil soluble sulfonates

and polyoxyethylene ethers 4%

xylene 66%

The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in packaging operation to insure the absence of any extraneous undissolved material in the product.

#### Example 55

#### Emulsifiable Concentrate

Butyl(4-chiorophenyl)methyl(1H-1,2,4-triazol-1-ylmethyl)silane

5 blend of oil soluble sulfonates

and polyoxyethylene ethers

4%

xylene

66%

The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in packaging operation to insure the absence of any extraneous undissolved material in the product.

#### Example 56

#### Emulsifiable Concentrate

bis(4-Chlorophenyl)methyl(1H-1,2,4-triazol-1-ylmethyl)silane

blend of oil soluble sulfonates

and polyoxyethylene ethers

4%

xylene

66%

The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in packaging operation to insure the absence of any extraneous undissolved material in the product.

#### Example 57

#### Emulsifiable Concentrate

bis(4-Fluorophenyl)methyl(lH-1,2,4-triazol-1-ylmethyl)silane
20%

chlorobenzene

74%

30 sorbitan monostearate and poly-

oxyethylene condensates thereof

The ingredients are combined and stirred to produce a solution which can be emulsified in water for application.

35

#### 110 .

#### Example 58

#### Emulsifiable Concentrate

4-Fluorophenyl(methyl)phenyl(lH-1,2,4-triazol-1-yl-methyl)silane 30%

5 blend of oil soluble sulfonates

and polyoxyethylene ethers 4%

xylene 66%

The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in packaging operation to insure the absence of any extraneous undissolved material in the product.

#### Example 59

#### Wettable Powder

15 (1,1'-Biphenyl-4-yl)dimethyl(lH-imidazol-l-ylmethyl)silane 50%

sodium alkylnaphthalenesulfonate 2% low viscosity methyl cellulose 2% diatomaceous earth 46%

The ingredients are blended, coarsely hammermilled and then air milled to produce particles of active essentially all below 10 microns in diameter. The product is reblended before packaging.

#### Example 60

#### 25 Wettable Powder

(1,1-Biphenyl-4-yl)dimethyl(lH-imidazol-l-ylmethyl)silane 40%

dioctyl sodium sulfosuccinate 1.5% sodium ligninsulfonate 3% low viscosity methyl cellulose 1.5% attapulgite 54%

The ingredients are thoroughly blended, passed through an air mill, to produce an average particle size under 15 microns, reblended, and sifted through a U.S.S. No. 50 sieve (0.3 mm opening) before packaging.

All compounds of the invention may be formulated in the same manner.

### Example 61

#### Emulsifiable Concentrate

(1,1'-8iphenyl-4-yl)dimethyl(lH-imidazol-l-ylmethyl)silane
30%

5 blend of oil soluble sulfonates

and polyoxyethylene ethers 4%

xylene 66%

The ingredients are combined and stirred with gentle warming to speed solution. A fine screen 10 filter is included in packaging operation to insure the absence of any extraneous undissolved material in the product.

#### Example 62

#### Emulsifiable Concentrate

15 (1,1'-8iphenyl-4-yl)dimethyl(lH-imidazol-l-ylmethyl)silane 20%

chlorobenzene 74%

sorbitan monostearate and poly-

oxyethylene condensates thereof 6%

The ingredients are combined and stirred to produce a solution which can be emulsified in water for application.

#### Example 63

#### Aqueous Suspension

25 (1,1'-Biphenyl-4-yl)dimethyl(lH-imidazol-l-ylmethyl)-silane 25%

hydrated attapulgite 3% crude calcium ligninsulfonate 10% sodium dihydrogen phosphate 0.5%

30 water 61.5%

The ingredients are ground together in a ball or roller mill until the solid particles have been reduced to diameters under 10 microns.

### Example 64

#### High Strength Concentrate

(1,1'-8iphenyl-4-yl)dimethyl(lH-imidazol-1-ylmethyl)silane 98.5%

5 silica aerogel

0.5%

synthetic amorphous fine silica

1.0%

The ingredients are blended and ground in a hammer-mill to produce a high strength concentrate essentially all passing a U.S.S. No. 50 sieve (0.3 mm openings). This material may then be formulated in a variety of ways.

#### Example 65

#### Granule

wettable powder of example 60 15%

gypsum 69%
potassium sulfate 16%

The ingredients are blended in a rotating mixer and water sprayed on to accomplish granulation. When most of the material has reached the desired range of 1.0 to 0.42 mm. (U.S.S. # 18 to 40 sieves), the granules are removed, dried, and screened. Oversize material is crushed to produce additional material in the desired range. These granules contain active ingredient.

Example 66

#### Dust

high strength concentrate from

Example 64 25.4% pyrophyllite, powdered 74.6%

The ingredients are thoroughly blended and packaged for use.

# Example 67

Emulsi	fiable	Concentrate	

4-Chlorophenyl(methyl)phenyl(lH-imidazol-l-yl-methyl)silane 20%

5 chlorobenzene

74%

sorbitan monostearate and polyoxyethylene condensates thereof 6% The ingredients are combined and stirred to

produce a solution which can be emulsified in water 10 for application.

15

20

25

30

#### Utility .

The compounds of this invention are useful as plant disease control agents. They are effective in controlling a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, vegetable, field, cereal and fruit crops, such as, <u>Puccinia recondita</u>, <u>Erysiphe cichoracearum</u>, <u>Erysiphe graminis</u>, <u>Venturia inaequalis</u>, <u>Helminthosporium maydis</u>, <u>Cercospora arachidicola</u>, <u>Uromyces phaseoli</u> and <u>Monilinia</u>

10 <u>fructicola</u>, <u>Rhizoctonia solani</u>, <u>Pyricularia oryzae</u>, <u>Phytophthora infestans</u> and other <u>Phytophthora</u> species. They also control seed pathogens such as Pythium aphanadermatum.

Oisease control is ordinarily accomplished by applying an effective amount of the compound either pre- or post-infection to the portion of the plant to be protected, such as the roots, stems, foliage, fruit, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. The compound may also be applied to the seed from which the plants to be protected are to be grown.

Rates of application for these compounds can be influenced by many factors of the environment and should be determined under actual use conditions.

25 Foliage can normally be protected when treated at a rate of from less than 1 to 500 ppm of active ingredient. Plants growing in soil treated at a concentration from 0.1 to about 20 kg/ha can be protected from disease. Seed and seedlings can normally be protected when seed is treated at a rate of from 0.06 to about 3 grams per kilogram of seed.

The compounds of this invention can be mixed with fungicides, bactericides, acaricides, nematicides, insecticides, or other biologically active compounds in order to achieve desired results with a minimum expenditure of time, effort and material.

Amounts of these biologically active materials added for each part by weight of the composition of this invention may vary from 0.05 to 25 parts by weight. Suitable agents of this type are well-known to those skilled in the art. Some are listed below:

#### Fungicides:

20

methyl 2-benzimidazolecarbamate (carbendazim) tetramethylthiuram disulfide (thiuram) n-dodecylguanidine acetate (dodine)

2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide
 (cymoxanil)

N-trichloromethylthiotetrahydrophthalimide (captan)
N-trichloromethylthiophthalimide (folpet)
dimethyl 4,4'-(o-phenylene)bis(3-thioallophanate)
(thiophanate-methyl)

25 2-(thiazol-4-yl)benzimidazole (thiabendazole)
aluminum tris(0-ethyl phosphonate) ("Aliette")
tetrachloroisophthalonitrile (chlorothalonil)
2,6-dichloro-4-nitroaniline (dichloran)
N-(2,6-dimethylphenyl)-N-(methoxyacetyl)alanine methyl
ester (metalaxyl)

cis-N-[(1,1,2,2-tetrachloroethyl)thio]cyclohex-4-ene1,2-dicarbioximide (captafol)

- 3-(3,5-dichlorophenyl)-N-(1-methylethyl)-2,4-dioxo-1-imidazolidine carboxamide (iprodione)
- 35 3-(3,5-dichlorophenyl)-5-ethenyl-5-methyl-2,4-oxazoli-dinedione (vinclozolin)

kasugamycin

O-ethyl-S,S-diphenylphosphorodithioate (edifenphos)

#### Bactericides:

tribasic copper sulfate

5 streptomycin sulfate

oxytetracycline

#### Acaricides:

senecioic acid, ester with 2-<u>sec</u>-butyl-4,6-dinitrophenol (binapacryl)

- 10 6-methyl-1,3-dithiolo[2,3-B]quinonolin-2-one (oxythioquinox)
  - 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol (dicofol)

bis(pentachloro-2,4-cyclopentadien-1-y1) (dienochlor)

15 tricyclohexyltin hydroxide (cyhexatin)

hexakis(2-methyl-2-phenylpropyl)distannoxane (fenbutin oxide)

#### Nematicides:

- 2-[diethoxyphosphinylimino]-1,3-dithietane (fosthietan)
- 20 S-methyl-l-(dimethylcarbamoyl)-N-(methylcarbamoyloxy)thioformimidate (oxamyl)
  - S-methyl-1-carbamoyl-N-(methylcarbamoyloxy)thioformimidate
  - N-isopropylphosphoramidic acid, 0-ethyl-0'-[4-(methyl-thio)-m-tolyl]diester (fenamiphos)

#### Insecticides:

25

- 3-hydroxy-N-methylcrotonamide(dimethylphosphate)ester (monocrotophos)
- methylcarbamic acid, ester with 2,3-dihydro-2,2-dimethyl-7-benzofuranol (carbofuran)
- $0-[2,4,5-trichloro-\alpha-(chloromethyl)benzyl]$ phosphoric acid, 0',0'-dimethyl ester (tetrachlorvinphos)
- 2-mercaptosuccinic acid, diethyl ester, S-ester with thionophosphoric acid, dimethyl ester (malathion)
- ophosphorothioic acid, 0,0-dimethyl, 0- $\underline{p}$ -nitrophenyl ester (methyl parathion)

```
methylcarbamic acid, ester with \alpha-naphthol (carbaryl)
   methyl N-[[(methylamino)carbonyl]oxy]ethanimidothioate
     (methomyl)
   N'-(4-chloro-o-toly1)-N, N-dimethylformamidine
     (chlordimeform)
   0,0-diethyl-0-(2-isopropyl-4-methyl-6-pyrimidyl)phos-
     phorothicate (diazinon)
   octachlorocamphene (toxaphene)
   O-ethyl O-p-nitrophenyl phenylphosphonothioate (EPN)
10 cyano(3-phenoxyphenyl)-methyl 4-chloro-α-(1-methyl-
     ethyl)benzeneacetate (fenvalerate)
   (3-phenoxyphenyl)methyl (+)-cis, trans-3-(2,2-dichloro-
     ethenyl)-2,2-dimethylcyclopropanecarboxylate
     (permethrin)
15 dimethyl N,N'-[thiobis](N-methylimino)carbonyloxy]]-
     bis[ethanimidothioate] (thiodicarb)
   phosphorothiolothionic acid, 0-ethyl-0-[4-(methylthio)-
     phenyl]-S-n-propyl ester (sulprofos)
   a-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-
     dimethylcyclopropane carboxylate (cypermethrin)
   cyano(3-phenoxyphenyl)methyl 4-(difluoromethoxy)-\alpha-
     (methylethyl)benzeneacetate ("Payoff")
   0,0-diethyl-0-(3,5,6-trichloro-2-pyridyl)phosphoro-
     thioate (chlorpyrifos)
0,0-dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3-(4H)-yl)-
     methyl]phosphorodithioate (azinphos-methyl)
    5,6-dimethyl-2-dimethylamino-4-pyrimidinyl dimethyl
     carbamate ("Pirimor")
    S-(N-formyl-N-methylcarbamoylmethyl)-0,0-dimethyl
     phosphorodithioate (formothion)
   S-2-(ethylthioethyl)-0,0-dimethyl phosphiorothioate
      (demeton-S-methyl)
   α-cyano-3-phenoxybenzyl cis-3-(2,2-dibromovinyl)-2,2-
     dimethylcyclopropane carboxylate (deltamethrin)
35 cyano(3-phenoxyphenyl)methyl ester of N-(2-chloro-4-
      trifluoromethylphenyl)alanine ("Mavrik")
```

This invention is further illustrated by the following examples.

#### Example 68

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume and then suspended at a concentration of 100 ppm in purified water containing 250 ppm of the surfactant TREM 014 (polyhydric alcohol esters). These suspensions were sprayed to the point of run-off on wheat seedlings. The following day, the plants were inoculated with a spore suspension of <u>Puccinia recondita</u> var. <u>tritici</u>, causal agent of wheat leaf rust, and incubated in a saturated humidity chamber at 20° for 24 hours and then in a growth room for an additional 7 days, when disease ratings were made. Percent disease control is shown in the following table. Treated plants had few or no rust pustules while the untreated plants had numerous rust pustules on each leaf.

20

#### Table 1

	Compound	% Control Wheat Rust
25	(Dimethyl)phenyl(1,2,4-triazol-1-ylmethyl)silane	90
	(4-8romophenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane	80
30	(1,1'-8iphenyl-4-yl)dimethyl(lH- 1,2,4-triazol-1-ylmethyl)silane	100
	(4-Chlorophenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane	100
	Butyl(4-chlorophenyl)methyl(lH- 1,2,4-triazol-l-ylmethyl)silane	80
35	<pre>(3,4-Dichlorophenyl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	60

	Compound %	Control Wheat Rust
5	<pre>(2,4-Dichlorophenyl)dimethyl(1H- l,2,4-triazol-l-ylmethyl)silane</pre>	90
	<pre>bis(4-Chlorophenyl)(methyl)(lH-     1,2,4-triazol-l-ylmethyl)silane</pre>	90
	Dimethyl(4-fluorophenyl)(1H-1,2,4- triazol-l-ylmethyl)silane	100
10	<pre>[4-(1,1-Dimethylethyl)phenyl]di- methyl(1H-1,2,4-triazol-1-yl- methyl)silane</pre>	80A
	Butyl(2,4-dichlorophenyl)methyl(1H- 1,2,4-triazol-l-ylmethyl)silane	100
15	bis(2,4-Dichlorophenyl)(methyl)(lH- l,2,4-triazol-l-ylmethyl)silane	100
	(2,4-Dichlorophenyl)methyl(phenyl)- (1H-1,2,4-triazol-1-ylmethyl)sila	ine 100
20	(4-Chlorophenyl)methyl(phenyl)(1H- 1,2,4-triazol-l-ylmethyl)silane	100
	(4-Fluorophenyl)methyl(phenyl)(lH- 1,2,4-triazol-l-ylmethyl)silane	90
	Dodecyl(dimethyl)(lH-1,2,4-triazol- l-ylmethyl)silane	100 <sup>A</sup>
25	[4-(4-Chlorophenoxy)phenyl]dimethyl (1H-1,2,4-triazol-1-ylmethyl)sila	
	<pre>(3,5-Dichlorophenyl)dimethyl(lH- 1,2,4-triazol-l-ylmethyl)silane</pre>	80
30	(1,1'-8iphenyl-4-yl)butyl(methyl)- (1H-1,2,4-triazol-1-ylmethyl)sila	ane 90
	<pre>bis(1,1'-Biphenyl-4-yl)(methyl)(lH- 1,2,4-triazol-1-ylmethyl)silane</pre>	80
	(1,1'-Biphenyl-4-yl)methyl(phenyl)- (1H-1,2,4-triazol-1-ylmethyl)sil:	
35	<pre>(1,1'-8ipheny1-3-y1)dimethy1(1H-1,:     triazol-1-ylmethy1)silane</pre>	2,4 <del>-</del> 80

## Table 1 (continued)

## Compound % Control Wheat Rust

5	<pre>2-Chlorophenyl(methyl)phenyl(1H-1,2,4- triazol-1-ylmethyl)silane</pre>	80	
	<pre>[bis(2-Chlorophenyl)]methyl(1H-1,2,4- triazol-1-ylmethyl)silane</pre>	100	
10	<pre>(1,1'-Biphenyl-4-yl)dimethyl(1H-1,2,4- triazol-1-ylmethyl)silane, 4-dodecyl- benzenesulfonic acid salt</pre>	100	
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1,2,4 triazol-l-ylmethyl)silane, 1:1 com- plex with zinc (II) chloride</pre>	100	
15	<pre>(1,1'-Biphenyl-4-yl)dimethyl(1H-1,2,4- triazol-1-ylmethyl)silane, 1:1 com- plex with manganous sulfate</pre>	90	
	2-Chlorophenyl(4-chlorophenyl)methyl- (1H-1,2,4-triazol-1-ylmethyl)silane	100	
20	<pre>[bis(2-Fluorophenyl)]methyl(lH-     1,2,4-triazol-l-ylmethyl)silane,     1:1 complex with cuprous chloride</pre>	90	
	<pre>[bis(2-Fluorophenyl)]methyl(lH-     1,2,4-triazol-l-ylmethyl)silane,     2:1 complex with cupric chloride</pre>	100	
25	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH- imidazol-l-ylmethyl)silane</pre>	100	
	(4-Chlorophenyl)(lH-imidazol-l- ylmethyl)dimethylsilane	50	
	Butyl(4-chlorophenyl)(lH-imidazol- l-ylmethyl)methylsilane	90	
30	<pre>(lH-Imidazol-l-ylmethyl)dimethyl-   (4-phenoxyphenyl)silane</pre>	60	
	Dimethyl(lH-imidazol-l-ylmethyl)- (4-methoxyphenyl)silane	60	
35	<pre>(2,4-Dichlorophenyl)dimethyl(lH- imidazol-l-ylmethyl)silane</pre>	90	

% Control Wheat Rust

# Table 1 (continued)

Compound

	<u>Compound</u>	
5	<pre>bis(4-Fluorophenyl)(lH-imidazol-l- ylmethyl)methylsilane</pre>	100
	Dimethyl(4-fluorophenyl)(lH-imida- zol-l-ylmethyl)silane	80
	Dimethyl(lH-imidazol-l-ylmethyl)- (4-trifluoromethylphenyl)silane	100 <sup>A</sup>
10	Butyl(2,4-dichlorophenyl)(lH-imida zol-1-ylmethyl)methylsilane	100
	<pre>bis(2,4-Dichlorophenyl)(1H-imidazo l-ylmethyl)methylsilane</pre>	1-
16	<pre>2,4-Dichlorophenyl(1H-imidazol-l- ylmethyl)methyl(phenyl)silane</pre>	<b>90</b>
15	4-Chlorophenyl(lH-imidazol-l-yl-methyl)methyl(phenyl)silane	100
	Dodecyl(dimethyl)(lH-imidazol-l- ylmethyl)silane	80 <sup>A</sup>
20	[4-(4-Chlorophenoxy)phenyl]dimethy (1H-imidazol-l-ylmethyl)silane	90
	<pre>Butyl(lH-imidazol-l-ylmethyl)- methyl(phenyl)silane</pre>	90
25	<pre>(1,1'-8iphenyl-4-yl)butyl(lH-imida zol-1-ylmethyl)methylsilane</pre>	100
25	(1,1'-8iphenyl-4-yl)(lH-imidazol- l-ylmethyl)methyl(phenyl)silane	100
	<pre>(1,1'-Biphenyl-3-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	90
30	<pre>(4-8romophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	90
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(1H- imidazol-l-ylmethyl)silane, 1:1 complex with cuprous chloride</pre>	100
35	<pre>(2-Chlorophenyl)(4-chlorophenyl)( imidazol-l-ylmethyl)methylsilan</pre>	1H- e 100

## Table 1 (continued)

## Compound

% Control Wheat Rust

(2-Chlorophenyl)(dimethyl)(lH-imidazol-l-ylmethyl)silane

A Compound applied at a concentration of 200 ppm.

### Example 69

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume and then suspended at a concentration of 100 ppm in 5 purified water containing 250 ppm of the surfactant TREM Ol4 (polyhydric alcohol esters). These suspensions were sprayed to the point of run-off on cucumber seedlings. The following day, the plants were inoculated with a spore suspension of the fungus Erysiphe 10 cichoracearum, causal agent of cucumber powdery mildew, and incubated in a growth room for 7 days. Disease ratings were then made. Percent disease control is shown in the following table. Treated plants had little or no powdery mildew in contrast to un-15 treated plants which were covered with powdery mildew. Phytotoxicity in the form of growth reduction or hormonal effects was observed on some of the plants in association with disease control.

20 Table 2

	Compound	% Control Cucumber Powdery Mildew
25	(Dimethyl)phenyl(1,2,4-triazol-l- ÿlmethyl)silane	100
	Ethyldimethyl(1H-1,2,4-triazol-1-ylmethyl)silane	100 .
30	<pre>Butyldimethyl(lH-1,2,4-triazol-1- ylmethyl)silane</pre>	100
	Dimethyl(4-methylphenyl)(1H-1,2,4-triazol-1-ylmethyl)silane	100G <sup>A</sup>
	<pre>(4-8romophenyl)dimethyl(1H-1,2,4- triazol-1-ylmethyl)silane</pre>	100G

124
Table 2 (continued)

	Compound	% Control Cucumber Powdery Mildew
5	<pre>(1,1'-Biphenyl-4-yl)dimethyl(lH- 1,2,4-triazol-1-ylmethyl)silane</pre>	100
	(4-Chlorophenyl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane	100
10	Butyl(4-chlorophenyl)methyl(1H- l,2,4-triazol-l-ylmethyl)silane	100G
	Dimethyl(l-naphthalenyl)(lH-1,2,4-triazol-l-ylmethyl)silane	100
	(3,4-Dichlorophenyl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane	100
15	Oimethyl(4-phenoxyphenyl)(1H-1,2,4-triazol-1-ylmethyl)silane	70
	Dimethyl(4-methoxyphenyl)(1H-1,2,4-triazol-1-ylmethyl)silane	100
20	(2,4-Dichlorophenyl)dimethyl(lH- 1,2,4-triazol-l-ylmethyl)silane	100HB
	<pre>bis(4-Chlorophenyl)(methyl)(lH-     1,2,4-triazol-l-ylmethyl)silane</pre>	100
	(lH-1,2,4-Triazol-1-ylmethyl)tri- phenylsilane	100
25	Methyldiphenyl(1H-1,2,4-triazol-1-ylmethyl)silane	100G
	(1,1'-8iphenyl-4-yl)dimethyl(4H- 1,2,4-triazol-4-ylmethyl)silane	90
30	<pre>bis(4-Fluorophenyl)(methyl)(lH-     1,2,4-triazol-1-ylmethyl)silane</pre>	100G
- •	Oimethyl(4-fluorophenyl)(1H-1,2,4- triazol-1-ylmethyl)silane	100G
	Dimethyl(4-methylthiophenyl)(1H- 1,2,4-triazol-l-ylmethyl)silane	100

	Compound	% Control Cucumber Powdery Mildew
5	Dimethyl(1H-1,2,4-triazol-1-yl-methyl)(4-trifluoromethylphenyl)-silane	100G
	<pre>Dimethyl(lH-1,2,4-triazol-l-yl- methyl)(3-trifluoromethylphenyl)- silane</pre>	100
10	Dimethyl(1H-1,2,4-triazol-1-yl- methyl)(2-trifluoromethylphenyl)- silane	100
	(2-Methoxyphenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane	- 100G
15	Butyl(2,4-dichlorophenyl)methyl(lH- 1,2,4-triazol-l-ylmethyl)silane	_ 100G
	<pre>bis(2,4-Dichlorophenyl)(methyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	- 100G
20	(2,4-Dichlorophenyl)methyl(phenyl)- (1H-1,2,4-triazol-1-ylmethyl)sila	<u>-</u> ane 100G
	(4-Chlorophenyl)methyl(phenyl)(lH- 1,2,4-triazol-l-ylmethyl)silane	100G
	(4-Fluorophenyl)methyl(phenyl)(lH- 1,2,4-triazol-l-ylmethyl)silane	100
25	Butyl(methyl)phenyl(lH-1,2,4-triazo l-ylmethyl)silane	100
	<pre>(2,3-Dimethoxyphenyl)dimethyl(1H- 1,2,4-triazol-l-ylmethyl)silane</pre>	100G
30	<pre>(2,6-Dimethoxyphenyl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100G
,,	Dodecyl(dimethyl)(1H-1,2,4-triazol- l-ylmethyl)silane	- 60 <sup>C</sup>
	(2-Chlorophenyl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane	100G
35	<pre>[4-(4-Chlorophenoxy)phenyl]dimethy   (lH-1,2,4-triazol-l-ylmethyl)sil</pre>	1- ane 80

# 12,6

# Table 2 (continued)

	Compound	Control Powdery	Cucumber Mildew
5	(1,1'-Biphenyl-4-yl)butyl(methyl)- (1H-1,2,4-triazol-1-ylmethyl)silar	ne 100	0
	Butyl(4-fluorophenyl)methyl(1H-1,2,4 triazol-1-ylmethyl)silane	100	D
10	<pre>bis(1,1'-Biphenyl-4-yl)(methyl)(lH- 1,2,4-triazol-1-ylmethyl)silane</pre>	100	0
	(1,1'-8iphenyl-4-yl)methyl(phenyl)- (1H-1,2,4-triazol-1-ylmethyl)silar	ne 100	ם
	<pre>(1,1-Dimethylethoxy)methyl(phenyl)-   (1H-1,2,4-triazol-1-ylmethyl)silar</pre>	ne 100	
15	<pre>Methyl(phenyl)(2-propoxy)(1H-1,2,4- triazol-1-ylmethyl)silane</pre>	100	
	<pre>(1,1'-8iphenyl-2-yl)dimethyl(lH-1,2, triazol-l-ylmethyl)silane</pre>	4-	)
20	<pre>2-Chlorophenyl(methyl)phenyl(lH-1,2,     triazol-l-ylmethyl)silane</pre>	4-	)
	4-Bromophenyl(methyl)phenyl(lH-1,2,4 triazol-1-ylmethyl)silane	100	
	<pre>[bis(2-Chlorophenyl)]methyl(lH-1,2,4 triazol-l-ylmethyl)silane</pre>		
25	Cyclohexyl(dimethyl)(lH-1,2,4-triazo l-ylmethyl)silane	100	)G
	<pre>[bis(4-8romopheny1)]methy1(1H-1,2,4- triazol-1-ylmethy1)silane</pre>	80	)G
30	<pre>(1,1'-8iphenyl-4-y1)dimethyl(lH-1,2, triazol-1-ylmethyl)silane, 4-dodec benzenesulfonic acid salt</pre>		)
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1,2, triazol-1-ylmethyl)silane, l:l com plex with cuprous chloride</pre>	4-	)
35	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1,2, triazol-l-ylmethyl)silane, 1:1 com plex with zinc (II) chloride</pre>	4-	ı

	Compound	% Control Powdery	
5	<pre>(1,1'-8iphenyl-4-y1)dimethyl(1H-1,2   triazol-1-y1methyl)silane, 1:1 co   plex with manganous sulfate</pre>		)
10	2-Chlorophenyl(4-chlorophenyl)methy (1H-1,2,4-triazol-1-ylmethyl)sila		)
10	Phenyl[bis(2-propoxy)](1H-1,2,4- triazol-1-ylmethyl)silane	100	)
	<pre>[bis(2-Fluorophenyl)]methyl(lH- l,2,4-triazol-l-ylmethyl)silane, l:l complex with cuprous chloride</pre>	100	)
15	<pre>[bis(2-Fluoropheny1)]methyl(lH- l,2,4-triazol-l-ylmethyl)silane, 2:1 complex with cupric chloride</pre>	100	)
	Dimethyl(lH-imidazol-I-ylmethyl)- phenylsilane	100	
20	Ethyl(lH-imidazol-l-ylmethyl)- dimethylsilane	100	
	Butyl(lH-imidazol-l-ylmethyl)- dimethylsilane	100	)
25	(lH-Imidazol-l-ylmethyl)dimethyl- (4-methylphenyl)silane	. 100	JG <sup>A</sup>
	(4-Bromophenyl)(lH-imidazol-l-yl-methyl)dimethylsilane	100	)
	<pre>(1,1'-Biphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	100	)
30	(4-Chlorophenyl)(lH-imidazol-l- ylmethyl)dimethylsilane	100	)
	<pre>Butyl(4-chlorophenyl)(1H-imidazol- l-ylmethyl)methylsilane</pre>	100	)G
35	<pre>(lH-Imidazol-l-ylmethyl)dimethyl- (l-naphthalenyl)silane</pre>	100	)
,,			

128
Table · 2 · (continued)

	Compound	% -	Control Powdery	Cucumber Mildew
5	(3,4-Dichlorophenyl)(lH-imidazol- l-ylmethyl)dimethylsilane		100	3 -
	(lH-Imidazol-l-ylmethyl)dimethyl- (4-phenoxyphenyl)silane		100	
10	Oimethyl(lH-imidazol-l-ylmethyl)- (4-methoxyphenyl)silane		100	0
	(2,4-Dichlorophenyl)dimethyl(lH- imidazol-l-ylmethyl)silane		100	онв
15	<pre>bis(4-Chlorophenyl)(lH-imidazol-l- ylmethyl)methylsilane</pre>		100	
	(1H-Imidazol-l-ylmethyl)triphenyl- silane		10	3
	Diphenyl(lH-imidazol-l-ylmethyl)- methylsilane		100	3
20	<pre>bis(4-Fluorophenyl)(lH-imidazol-l- ylmethyl)methylsilane</pre>		100	0
	Dimethyl(4-fluorophenyl)(lH-imida- zol-l-ylmethyl)silane		10	og
	Dimethyl(lH-imidazol-l-ylmethyl)- (4-methylthiophenyl)silane		10	0
25	Dimethyl(lH-imidazol-l-ylmethyl)- (4-trifluoromethylphenyl)silane	•	10	o
	Oimethyl(lH-imidazol-l-ylmethyl)- (3-trifluoromethylphenyl)silane		8	0
30	[4-(1,1-Dimethylethyl)phenyl](1H- imidazol-l-ylmethyl)dimethylsila	ne	81	
	(lH-Imidazol-l-ylmethyl)dimethyl- (2-trifluoromethylphenyl)silane		10	og
35	Buty1(2,4-dichlorophenyl)(lH-imida- zol-l-ylmethyl)methylsilane	-	10	og

	Compound	% Control Cucumber Powdery Mildew
5	bis(2,4-Dichlorophenyl)(lH-imidazol l-ylmethyl)methylsilane	100
	(2,4-Dichlorophenyl)(lH-imidazol-l-ylmethyl)methyl(phenyl)silane	100
10	<pre>(4-Chlorophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	100
	<pre>(4-Fluorophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	100
	(lH-Imidazol-l-ylmethyl)(2-methoxy- phenyl)dimethylsilane	100G .
15	(2,3-Dimethoxyphenyl)(1H-imidazol- l-ylmethyl)dimethylsilane	100
	Dodecyl(dimethyl)(lH-imidazol-l- ylmethyl)silane	55
20	(2-Chlorophenyl)(lH-imidazol-l-yl-methyl)dimethylsilane	100
	[4-(4-Chlorophenoxy)phenyl]dimethyl (lH-imidazol-l-ylmethyl)silane	100
	Butyl(lH-imidazol-l-ylmethyl)- methyl(phenyl)silane	100
25	<pre>(1,1'-Biphenyl-4-yl)butyl(lH-imida- zol-1-ylmethyl)methylsilane</pre>	100
	Butyl(4-fluorophenyl)(lH-imidazol- l-ylmethyl)methylsilane	100
30	Oibutyl(lH-imidazol-l-ylmethyl)- methylsilane	100
	<pre>(1,1'-Biphenyl-4-yl)(lH-imidazol- l-ylmethyl)methyl(phenyl)silane</pre>	100
<b>3</b>	<pre>(1,1-Dimethylethoxy)(lH-imidazol-l- ylmethyl)methyl(phenyl)silane</pre>	100

Table 2 (continued)

	Compound	% —	Control Powdery	Cucumber Mildew
5	(lH-Imidazol-l-ylmethyl)methyl- (phenyl)(2-propoxy)silane		90	
	<pre>(lH-Imidazol-l-ylmethyl)[bis(4- methoxyphenyl)]methylsilane</pre>		50	2
10	(1,1'-Biphenyl-2-yl)dimethyl(lH- imidazol-l-ylmethyl)silane		50	)
	<pre>(2-Chlorophenyl)(IH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	•	100	
16	<pre>(4-Bromophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>		100	)
15	[bis(2-Chlorophenyl)](lH-imidazol- l-ylmethyl)methylsilane		100	)
	Cyclohexyl(dimethyl(lH-imidazol-l-ylmethyl)silane		. 100	og
20	[bis(4-8romophenyl)](1H-imidazol-l-ylmethyl)methylsilane	•	100	ם
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane, 1:1 complex with cuprous chloride</pre>		100	)
25	(2-Chlorophenyl)(4-chlorophenyl)(li imidazol-l-ylmethyl)methylsilane	<b>-</b>	100	
	(2-Chlorophenyl)(dimethyl)(lH-imi-dazol-l-ylmethyl)silane		80	נ
	AG = growth reduction; and BH = hormonal effects.			

### Example 70

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume and then suspended at a concentration of 100 ppm in 5 purified water containing 250 ppm of the surfactant TREM 014 (polyhydric alcohol esters). These suspensions were sprayed to the point of run-off on barley seedlings. The following day, the plants were inoculated with a spore suspension of the fungus Erysiphe 10 graminis, causal agent of barley powdery mildew, and incubated in a growth room for 7 days. Disease ratings were then made. Percent disease control is shown in the following table. Treated plants had little or no powdery mildew in contrast to untreated plants which were covered with powdery mildew.

#### Table 3

20	Compound	% Control Barley Powdery Mildew
20	Butyl(4-chlorophenyl)methyl(lH- 1,2,4-triazol-l-ylmethyl)silane	90
	(3,4-Dichlorophenyl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane	100
25	Dimethyl(4-methoxyphenyl)(1H-1,2,4-triazol-l-ylmethyl)silane	. 100
	<pre>(2,4-Dichlorophenyl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100
30	<pre>bis(4-Chlorophenyl)(methyl)(1H- 1,2,4-triazol-l-ylmethyl)silane</pre>	100
20	(lH-1,2,4-Triazol-1-ylmethyl)tri- phenylsilane	100
	Methyldiphenyl(1H-1,2,4-triazol-1-ylmethyl)silane	100
35	Oimethyl(1H-1,2,4-triazol-1-yl- methyl)(2-trifluoromethylphenyl)- silane	100

	Compound	% Control Barley Powdery Mildew
5	Dodecyl(dimethyl)(1H-1,2,4-triazol- l-ylmethyl)silane	100 <sup>A</sup>
	Butyl(4-chlorophenyl)(1H-imidazol- l-ylmethyl)methylsilane	100
10	(3,4-Dichlorophenyl)(lH-imidazol- l-ylmethyl)dimethylsilane	80
	Oimethyl(lH-imidazol-l-ylmethyl)- (4-methoxyphenyl)silane	100
	(2,4-Dichlorophenyl)dimethyl(lH- imidazol-l-ylmethyl)silane	100
15	<pre>bis(4-Chlorophenyl)(lH-imidazol-l- ylmethyl)methylsilane</pre>	100
	<pre>Diphenyl(lH-imidazol-l-ylmethyl)-   methylsilane</pre>	100
20	Dimethyl(lH-imidazol-l-ylmethyl)- (4-trifluoromethylphenyl)silane	100
	Dodecyl(dimethyl)(lH-imidazol-l- ylmethyl)silane	100 <sup>A</sup>

A Compound applied at a concentration of 200 ppm.

.25

#### Example 71

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume and then suspended at a concentration of 100 ppm in 5 purified water containing 250 ppm of the surfactant TREM 014 (polyhydric alcohol esters). These suspensions were sprayed to the point of run-off on apple seedlings. The following day, the plants\_were inoculated with a spore suspension of the fungus Venturia 10 inaequalis, causal agent of apple scab, and incubated in a saturated humidity chamber at 20° for 24 hours and then in a growth room for an additional 10-12 days. Disease ratings were then made and recorded as shown in the following table. Treated plants had 15 fewer apple scab lesions when compared to untreated plants which were covered with scab lesions. Phytotoxicity expressed as growth reduction was observed on some of the plants in association with disease control.

20

#### Table 4

	Compound	<u>%</u>	Control	Apple	Scab
25	Dimethyl(4-methylphenyl)(1H-1,2,4- triazol-1-ylmethyl)silane	•	:	50G <sup>A</sup>	
	(4-Bromophenyl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane		9	90G	
30	(1,1'-8iphenyl-4-yl)dimethyl(lH- 1,2,4-triazol-1-ylmethyl)silane		10	00	
	(4-Chlorophenyl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane	•	10	00	
	<pre>8utyl(4-chlorophenyl)methyl(1H- 1,2,4-triazol-l-ylmethyl)silane</pre>		10	oog	
35	<pre>Dimethyl(l-naphthalenyl)(lH-1,2,4- triazol-1-ylmethyl)silane</pre>	•	:	50	

	Compound % C	ontrol Apple Scab
5	(3,4-Dichlorophenyl)dimethyl(1H- 1,2,4-triazol-l-ylmethyl)silane	80
	<pre>Dimethyl(4-phenoxyphenyl)(1H-1,2,4- triazol-1-ylmethyl)silane</pre>	100
10	Dimethyl(4-methoxyphenyl)(1H-1,2,4- triazol-1-ylmethyl)silane	100
	<pre>(2,4-Dichlorophenyl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100
•	<pre>bis(4-Chlorophenyl)(methyl)(1H- 1,2,4-triazol-1-ylmethyl)silane</pre>	100
15	Methyldiphenyl(1H-1,2,4-triazol-1-ylmethyl)silane	100
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(4H- 1,2,4-triazol-4-ylmethyl)silane</pre>	80
20	<pre>bis(4-Fluorophenyl)(methyl)(1H- l,2,4-triazol-l-ylmethyl)silane</pre>	100
20	Dimethyl(4-fluorophenyl)(1H-1,2,4- triazol-1-ylmethyl)silane	80CB
	Dimethyl(4-methylthiophenyl)(1H- 1,2,4-triazol-1-ylmethyl)silane	60
25	Oimethyl(1H-1,2,4-triazol-1-ylmethyl) (2-trifluoromethylphenyl)silane	- 65GA,C
•	(2-Methoxyphenyl)dimethyl(lH-1,2,4-triazol-l-ylmethyl)silane	80
70	Butyl(2,4-dichlorophenyl)methyl(lH- 1,2,4-triazol-l-ylmethyl)silane	100G
30	<pre>bis(2,4-Dichlorophenyl)(methyl)(lH- 1,2,4-triazol-l-ylmethyl)silane</pre>	100
	(2,4-Dichlorophenyl)methyl(phenyl)- (1H-1,2,4-triazol-1-ylmethyl)silane	e 100G
35	(4-Chlorophenyl)methyl(phenyl)(lH- 1.2.4-triazol-l-ylmethyl)silane	100

# Table 4 (continued)

	<u>Compound</u>	Control	Apple Scab
5	(4-Fluorophenyl)methyl(phenyl)(lH- 1,2,4-triazol-l-ylmethyl)silane		100
	<pre>Butyl(methyl)phenyl(lH-1,2,4-triazo l-ylmethyl)silane</pre>	1-	80
	Oodecyl(dimethyl)(1H-1,2,4-triazol- l-ylmethyl)silane	•	408C,D
10	(2-Chlorophenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane		100
	[4-(4-Chlorophenoxy)phenyl]dimethy (1H-1,2,4-triazol-1-ylmethyl)sil	l- ane	100
15	(1,1'-8iphenyl-4-yl)butyl(methyl)- (1H-1,2,4-triazol-1-ylmethyl)sil	ane	80
	<pre>Butyl(4-fluorophenyl)methyl(1H-1,2   triazol-1-ylmethyl)silane</pre>	, 4-	100
	(1,1'-8iphenyl-4-yl)methyl(phenyl) (1H-1,2,4-triazol-1-ylmethyl)sil	- ane	100
20	<pre>(1,1'-Biphenyl-2-yl)dimethyl(1H-1,     triazol-1-ylmethyl)silane</pre>	2,4-	60
	<pre>(1,1'-Biphenyl-3-yl)dimethyl(1H-1, triazol-1-ylmethyl)silane</pre>	2,4-	50
25	<pre>2-Chlorophenyl(methyl)phenyl(lH-1, triazol-1-ylmethyl)silane</pre>	2,4-	90
	4-Bromophenyl(methyl)phenyl(lH-1,2 triazol-1-ylmethyl)silane	, 4-	100
	<pre>[bis(2-Chlorophenyl)]methyl(1H-1,2 triazol-l-ylmethyl)silane</pre>	, 4-	40
30	<pre>[bis(4-Bromophenyl)]methyl(lH-1,2, triazol-1-ylmethyl)silane</pre>	4-	80
	<pre>(1,1'-Biphenyl-4-yl)dimethyl(lH-1, triazol-1-ylmethyl)silane, 4-dod benzenesulfonic acid salt</pre>	2,4- lecy1-	100

# Compound % Control Apple Scab

5	(1,1'-Biphenyl-4-yl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane, 1:1 complex with cuprous chloride	100 .
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1,2,4- triazol-l-ylmethyl)silane, l:l com- plex with zinc (II) chloride</pre>	100
10	(1,1'-Biphenyl-4-yl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane, 1:1 complex with manganous sulfate	100
	2-Chlorophenyl(4-chlorophenyl)methyl- (1H-1,2,4-triazol-1-ylmethyl)silane	90
15	2-Chlorophenyl(dimethyl)(1H-1,2,4- triazol-1-ylmethyl)silane	60
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(1H- imidazol-1-ylmethyl)silane</pre>	80
20	Butyl(4-chlorophenyl)(1H-imidazol- l-ylmethyl)methylsilane	90
20	(lH-Imidazol-l-ylmethyl)dimethyl- (l-naphthalenyl)silane	40
	(3,4-Dichlorophenyl)(lH-imidazol- l-ylmethyl)dimethylsilane	80
25	(lH-Imidazol-l-ylmethyl)dimethyl- (4-phenoxyphenyl)silane	100
	<pre>(2,4-Dichlorophenyl)dimethyl(lH- imidazol-l-ylmethyl)silane</pre>	100
30	Diphenyl(lH-imidazol-l-ylmethyl)- methylsilane	50
	<pre>bis(4-Fluorophenyl)(lH-imidazol-l- ylmethyl)methylsilane</pre>	100
	Dimethyl(lH-imidazol-l-ylmethyl)- (4-trifluoromethylphenyl)silane	60 <sup>C</sup>
35	<pre>[4-(1,1-Dimethylethyl)phenyl](lH- imidazol-l-ylmethyl)dimethylsilane</pre>	50

## Compound

## % Control Apple Scab

Butyl(2,4-dichlorophenyl)(lH-imida- zol-l-ylmethyl)methylsilane	1008
<pre>bis(2,4-Dichlorophenyl)(lH-imidazol- l-ylmethyl)methylsilane</pre>	40
<pre>(2,4-Dichlorophenyl)(lH-imidazol-l- ylmethyl)methyl(phenyl)silane</pre>	80
(4-Chlorophenyl)(lH-imidazol-l-yl-methyl)methyl(phenyl)silane	100
<pre>(4-Fluorophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	100
(lH-Imidazol-l-ylmethyl)(2-methoxy- phenyl)dimethylsilane	60
(2-Chlorophenyl)(lH-imidazol-l-yl-methyl)dimethylsilane	90
<pre>Butyl(lH-imidazol-l-ylmethyl)- methyl(phenyl)silane</pre>	80
<pre>(1,1'-8iphenyl-4-yl)butyl(1H-imida- zol-1-ylmethyl)methylsilane</pre>	100
Butyl(4-fluorophenyl)(lH-imidazol- l-ylmethyl)methylsilane	80
Dibutyl(lH-imidazol-l-ylmethyl)- methylsilane	30
<pre>bis(1,1'-8iphenyl-4-yl)(lH-imi- dazol-1-ylmethyl)methylsilane</pre>	50
(lH-Imidazol-l-ylmethyl)[bis(4-methoxyphenyl)]methylsilane	50
<pre>(1,1'-8iphenyl-2-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	90
<pre>(1,1'-8iphenyl-3-yl)dimethyl(1H- imidazol-1-ylmethyl)silane</pre>	90
(2-Chlorophenyl)(lH-imidazol-l-yl-methyl)methyl(phenyl)silane	100
	zol-l-ylmethyl)methylsilane  bis(2,4-Dichlorophenyl)(lH-imidazol- l-ylmethyl)methylsilane  (2,4-Dichlorophenyl)(lH-imidazol-l- ylmethyl)methyl(phenyl)silane  (4-Chlorophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane  (4-Fluorophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane  (1H-Imidazol-l-ylmethyl)(2-methoxy- phenyl)dimethylsilane  (2-Chlorophenyl)(lH-imidazol-l-yl- methyl)dimethylsilane  8utyl(lH-imidazol-l-ylmethyl)- methyl(phenyl)silane  (1,1'-8iphenyl-4-yl)butyl(lH-imida- zol-l-ylmethyl)methylsilane  Butyl(4-fluorophenyl)(lH-imidazol- l-ylmethyl)methylsilane  Dibutyl(lH-imidazol-l-ylmethyl)- methylsilane  bis(1,1'-8iphenyl-4-yl)(lH-imi- dazol-l-ylmethyl)methylsilane  (1H-Imidazol-l-ylmethyl)[bis(4- methoxyphenyl)]methylsilane  (1,1'-8iphenyl-2-yl)dimethyl(lH- imidazol-l-ylmethyl)silane  (1,1'-8iphenyl-3-yl)dimethyl(lH- imidazol-l-ylmethyl)silane  (2-Chlorophenyl)(lH-imidazol-l-yl-

	Compound	% Control	Apple Scat	!
5	(4-Bromophenyl)(lH-imidazol-l-yl-methyl)methyl(phenyl)silane		30	
	[bis(2-Chlorophenyl)](1H-imidazol- 1-ylmethyl)methylsilane	-	<u>ė</u> 0	
10	Oimethyl(lH-imidazol-l-ylmethyl)- (4-methylsulfonylphenyl)silane		80	
	Cyclohexyl(dimethyl(lH-imidazol-lylmethyl)silane	-	1008	
	<pre>[bis(4-8romophenyl)](lH-imidazol- ylmethyl)methylsilane</pre>	1	50	
15	<pre>(1,1'-Biphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane, 1:1 complex with cuprous chloride</pre>		100	
	(2-Chlorophenyl)(4-chlorophenyl)( imidazol-l-ylmethyl)methylsilan	1H- e .	80	
20	<pre>(lH-Imidazol-l-ylmethyl)phenyl- [bis(2-propoxy)]silane</pre>		70	
	(2-Chlorophenyl)(dimethyl)(1H-imidazol-l-ylmethyl)silane	, <b></b>	60	
25	AG = growth reduction. BC = chlorosis. Commound applied at a concentrat	ion of 400	ppm.	

#### Example 72

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume and then suspended at a concentration of 100 ppm in 5 purified water containing 250 ppm of the surfactant TREM 014 (polyhydric alcohol esters). These suspensions were sprayed to the point of run-off on corn seedlings. The following day, the plants were inoculated with a spore suspension of Helminthosporium 10 maydis, causal agent of southern corn leaf blight, and incubated in a saturated humidity chamber at 20° for 24 hours and then in a growth room for an additional 7 days, when disease ratings were made. Percent disease control is shown in the following 15 table. Treated plants had few or no lesions while the untreated plants had numerous lesions on each leaf. Phytotoxicity expressed as growth reduction was observed on some of the plants in association with disease control.

20

#### Table 5

	Compound	% —	Control of Southern Corn Leaf Blight
25	(4-Bromophenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane		90
	(1,1'-8iphenyl-4-yl)dimethyl(1H- 1,2,4-triazol-1-ylmethyl)silane		90
30	(3,4-Dichlorophenyl)dimethyl(lH- 1,2,4-triazol-l-ylmethyl)silane		90
	Dimethyl(4-methoxyphenyl)(1H-1,2,4 triazol-1-ylmethyl)silane	-4	90
	(2,4-Dichlorophenyl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane		90
35	<pre>bis(4-Chlorophenyl)(methyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>		80

# Table 5 (continued)

	Compound	% Control of Southern Corn Leaf Blight
5	Methyldiphenyl(lH-1,2,4-triazol-1-ylmethyl)silane	80 .
10	(1,1'-Biphenyl-4-yl)dimethyl(4H- 1,2,4-triazol-4-ylmethyl)silane	100
	<pre>bis(4-Fluorophenyl)(methyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100
	<pre>Dimethyl(4-fluorophenyl)(1H-1,2,4- triazol-l-ylmethyl)silane</pre>	90
15	Oimethyl(4-methylthiophenyl)(lH- 1,2,4-triazol-l-ylmethyl)silane	80
	<pre>Dimethyl(1H-1,2,4-triazol-1-yl- methyl)(4-trifluoromethylphenyl) silane</pre>	<b>-</b> 50
20	<pre>[4-(1,1-Dimethylethyl)phenyl]di- methyl(1H-1,2,4-triazol-1-yl- methyl)silane</pre>	60
	(2-Methoxyphenyl)dimethyl(lH-1,2,4 triazol-l-ylmethyl)silane	70
	<pre>Butyl(2,4-dichlorophenyl)methyl(lH l,2,4-triazol-l-ylmethyl)silane</pre>	100
25	<pre>bis(2,4-Dichlorophenyl)(methyl)(1H     1,2,4-triazol-1-ylmethyl)silane</pre>	80
30.	(4-Chlorophenyl)methyl(phenyl)(1H- 1,2,4-triazol-1-ylmethyl)silane	90
	<pre>(4-Fluorophenyl)methyl(phenyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	90
	(2-Chlorophenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane	100 .
	[4-(4-Chlorophenoxy)phenyl]dimethy (1H-1,2,4-triazol-1-ylmethyl)sil	
35	<pre>(3,5-Dichlorophenyl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	40

# Table 5 (continued)

	% Compound	Control of Southern Corn Leaf Blight
5	· ·	
J	(1,1'-8iphenyl-4-yl)butyl(methyl)- (1H-1,2,4-triazol-1-ylmethyl)sila	ne 50
·	(1,1'-8iphenyl-4-y1)methyl(phenyl)- (1H-1,2,4-triazol-1-ylmethyl)sila	ne 90
10	<pre>[bis(4-Methoxyphenyl)]methyl(lH-1,2 triazol-l-ylmethyl)silane</pre>	,4- 90
ì	<pre>(1,1'-Biphenyl-2-yl)dimethyl(1H-1,2 triazol-1-ylmethyl)silane</pre>	,4 <b>-</b> 90
15	<pre>(1,1'-Biphenyl-3-yl)dimethyl(lH-1,2 triazol-l-ylmethyl)silane</pre>	,4-
	<pre>2-Chlorophenyl(methyl)phenyl(1H-1,2 triazol-l-ylmethyl)silane</pre>	,4 <b>-</b>
	4-Bromophenyl(methyl)phenyl(lH-1,2, triazol-l-ylmethyl)silane	4 <b>-</b> 80
20	<pre>[bis(2-Chlorophenyl)]methyl(1H-1,2,     triazol-l-ylmethyl)silane</pre>	4 <b>-</b> 60
	Cyclohexyl(dimethyl)(1H-1,2,4-triaz l-ylmethyl)silane	ol- 50
25	<pre>(1,1'-Biphenyl-4-yl)dimethyl(1H-1,2   triazol-1-ylmethyl)silane, 4-dode   benzenesulfonic acid salt</pre>	
	(1,1'-Biphenyl-4-yl)dimethyl(1H-1,2 triazol-1-ylmethyl)silane, 1:1 co plex with cuprous chloride	
30	(1,1'-Biphenyl-4-yl)dimethyl(lH-1,2 triazol-1-ylmethyl)silane, 1:1 copplex with zinc (II) chloride	,4 <b>-</b> m- 90
	<pre>(1,1'-8iphenyl-4-yl)dimethyI(lH-1,2   triazol-l-ylmethyl)silane, 1:1 co   plex with manganous sulfate</pre>	
35	2-Chlorophenyl(4-chlorophenyl)methy (1H-1,2,4-triazol-1-ylmethyl)sila	l- ne 60

# Table 5 (continued)

	Compound	% Control of Southern Corn Leaf Blight
5	(1,1'-8iphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane	90
	Butyl(4-chlorophenyl)(lH-imidazol- l-ylmethyl)methylsilane	50
10	(3,4-Dichlorophenyl)(lH-imidazol- l-ylmethyl)dimethylsilane	70
	(2,4-Dichlorophenyl)dimethyl(lH- imidazol-l-ylmethyl)silane	70
	bis(4-Chlorophenyl)(lH-imidazol-l-ylmethyl)methylsilane	60
15	(1H-Imidazol-l-ylmethyl)triphenyl- silane	50
	Diphenyl(lH-imidazol-l-ylmethyl)- methylsilane	60
20	bis(4-Fluorophenyl)(lH-imidazol-l-ylmethyl)methylsilane	. 60
	[4-(1,1-Oimethylethyl)phenyl](lH-imidazol-l-ylmethyl)dimethylsila	ine 70
	(lH-Imidazol-l-ylmethyl)dimethyl- (2-trifluoromethylphenyl)silane	90
25	Butyl(2,4-dichlorophenyl)(lH-imida zol-l-ylmethyl)methylsilane	80
	bis(2,4-Dichlorophenyl)(lH-imidazo	80
30	(4-Fluorophenyl)(lH-imidazol-l-yl-methyl)methyl(phenyl)silane	80
	<pre>(2,6-Dimethoxyphenyl)(dimethyl)(l} imidazol-l-ylmethyl)silane</pre>	f <b>-</b> 50
	<pre>Dibutyl(lH-imidazol-l-ylmethyl)-   methylsilane</pre>	, . 90

# 143 Table 5 (continued)

	Compound	% Control of Southern Corn Leaf Blight
5	(1,1'-8iphenyl-4-yl)(lH-imidazol- l-ylmethyl)methyl(phenyl)silane	80
	<pre>(1,1'-Biphenyl-3-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	90
10	<pre>[bis(2-Chlorophenyl)](lH-imidazol- l-ylmethyl)methylsilane</pre>	90
	Cyclohexyl(dimethyl(lH-imidazol-l-ylmethyl)silane	50

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume and then suspended at a concentration of 100 ppm in 5 purified water containing 250 ppm of the surfactant TREM 014 (polyhydric alcohol esters). These suspensions were sprayed to the point of run-off on peanut seedlings. The following day, the plants were inoculated with a spore suspension of Cercospora arachi-10 dicola, causal agent of peanut early leafspot, and incubated in a saturated humidity chamber at 27° for 24 hours and then in a growth room for an additional 14 days, when disease ratings were made. The results are shown in the following table. Treated plants had 15 few or no leafspots while the untreated plants had numerous leafspots. Phytotoxicity expressed as burn was observed in association with disease control for some treated plants.

	Compound	% Control Peanut Early Leafspot
2 <i>5</i>	<pre>bis(4-Chlorophenyl)(methyl)(lH-     1,2,4-triazol-l-ylmethyl)silane</pre>	100
	Methyldiphenyl(1H-1,2,4-triazol-1-ylmethyl)silane	100
30	<pre>(1,1'-8iphenyl-4-y1)dimethyl(1H- 1,2,4-triazol-1-ylmethyl)silane</pre>	100
	<pre>(4-Chlorophenyl)dimethyl(1H-1,2,4- triazol-1-ylmethyl)silane</pre>	90
	Dimethyl(l-naphthalenyl)(lH-1,2,4-triazol-1-ylmethyl)silane	90
35	<pre>(2,4-Dichlorophenyl)dimethyl(1H- l,2,4-triazol-l-ylmethyl)silane</pre>	100

145
Table 6 (continued)

	Compound	% Control Peanut Early Leafspot
-		
5	<pre>bis(4-Fluorophenyl)(methyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100
	Dimethyl(4-fluorophenyl)(1H-1,2,4- triazol-1-ylmethyl)silane	50
10	<pre>[4-(1,1-Dimethylethyl)phenyl]di- methyl(1H-1,2,4-triazol-1-yl- methyl)silane</pre>	35
	Oimethyl(lH-1,2,4-triazol-1-yl-methyl)(2-trifluoromethylphenyl)-silane	25B
15	Butyl(2,4-dishlorophenyl)methyl(lH- l,2,4-triazol-l-ylmethyl)silane	100
	<pre>bis(2,4-Dichlorophenyl)(methyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100
20	(2,4-Dichlorophenyl)methyl(phenyl)- (1H-1,2,4-triazol-1-ylmethyl)silar	ne 100
	<pre>(4-Chlorophenyl)methyl(phenyl)(1H- l,2,4-triazol-l-ylmethyl)silane</pre>	100
•	<pre>(4-Fluorophenyl)methyl(phenyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100
25	(2-Chlorophenyl)dimethyl(1H-1,2,4- triazol-1-ylmethyl)silane	. 30
	(1,1'-Biphenyl-4-yl)butyl(methyl)- (1H-1,2,4-triazol-1-ylmethyl)silar	ne 100
30	<pre>bis(1,1'-8iphenyl-4-yl)(methyl)(lH- 1,2,4-triazol-1-ylmethyl)silane</pre>	80
	(1,1'-8iphenyl-4-yl)methyl(phenyl)- (1H-1,2,4-triazol-1-ylmethyl)silar	ne 100
	<pre>[bis(4-Methoxyphenyl)]methyl(1H-1,2, triazol-1-ylmethyl)silane</pre>	, 4 <b>-</b> 30
35	<pre>(1,1'-8iphenyl-2-yl)dimethyl(1H-1,2, triazol-1-ylmethyl)silane</pre>	, 4 <b>-</b> 100

# 146 Table 6 (continued)

	Compound	% Control Peanut Early Leafspot
_		
5	(1,1'-8iphenyl-3-yl)dimethyl(1H-1,2,4 triazol-1-ylmethyl)silane	4 <b>-</b> 90
	2-Chlorophenyl(methyl)phenyl(lH-1,2,4 triazol-1-ylmethyl)silane	100
10	4-Bromophenyl(methyl)phenyl(1H-1,2,4-triazol-1-ylmethyl)silane	100
	[bis(2-Chlorophenyl)]methyl(1H-1,2,4-triazol-1-ylmethyl)silane	100
15	<pre>[bis(4-Bromophenyl)]methyl(1H-1,2,4- triazol-l-ylmethyl)silane</pre>	100
	<pre>(1,1'-Biphenyl-4-yl)dimethyl(lH-1,2, triazol-1-ylmethyl)silane, 4-dodec benzenesulfonic acid salt</pre>	
20	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1,2, triazol-1-ylmethyl)silane, 1:1 com plex with cuprous chloride</pre>	100
	<pre>(1,1'-Biphenyl-4-yl)dimethyl(lH-1,2, triazol-1-ylmethyl)silane, 1:1 com- plex with zinc (II) chloride</pre>	
25	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1,2, triazol-1-ylmethyl)silane, l:l com plex with manganous sulfate</pre>	
	2-Chlorophenyl(4-chlorophenyl)methyl (1H-1,2,4-triazol-1-ylmethyl)silan	
30	<pre>[bis(2-Fluorophenyl)]methyl(lH- 1,2,4-triazol-l-ylmethyl)silane, l:l complex with cuprous chloride</pre>	100
	<pre>[bis(2-Fluorophenyl)]methyl(1H- 1,2,4-triazol-l-ylmethyl)silane, 2:1 complex with cupric chloride</pre>	100
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	100

147
Table 6 (continued)

	Compound	% Control Peanut Early Leafspot
5	(2,4-Dichlorophenyl)dimethyl(lH- imidazol-l-ylmethyl)silane	100
	Diphenyl(lH-imidazol-l-ylmethyl)- methylsilane	50
10	<pre>bis(4-Fluorophenyl)(lH-imidazol-l- ylmethyl)methylsilane</pre>	100
	Dimethyl(4-fluorophenyl)(lH-imida- zol-l-ylmethyl)silane	608 <sup>A</sup>
1 e	Dimethyl(lH-imidazol-l-ylmethyl)- (4-trifluoromethylphenyl)silane	36 <sup>B</sup>
15	Oimethyl(lH-imidazol-l-ylmethyl)- (3-trifluoromethylphenyl)silane	50
	<pre>8utyl(2,4-dichlorophenyl)(lH-imida- zol-l-ylmethyl)methylsilane</pre>	100
20	<pre>bis(2,4-Dichlorophenyl)(lH-imidazol- l-ylmethyl)methylsilane</pre>	, 90
	(2,4-Dichlorophenyl)(lH-imidazol-l-ylmethyl)methyl(phenyl)silane	100
25	<pre>(4-Chlorophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	100
23	(4-Fluorophenyl)(lH-imidazol-l-yl-methyl)methyl(phenyl)silane	100
•	(2-Chlorophenyl)(1H-imidazol-l-yl-methyl)dimethylsilane	80
30	(1,1'-8iphenyl-4-yl)butyl(lH-imida-zol-1-ylmethyl)methylsilane	90
	<pre>bis(1,1'-Biphenyl-4-yl)(lH-imi- dazol-1-ylmethyl)methylsilane</pre>	60
35	<pre>(1,1'-8iphenyl-4-yl)(lH-imida- zol-1-ylmethyl)methyl(phenyl)- silane</pre>	80

148
Table 6 (continued)

•	Compound	% Control Pt Early Leafs
	<pre>(1,1'-8iphenyl-2-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	, *
	<pre>(1,1'-Biphenyl-3-yl)dimethyl(lH- imidazol-l-ylmethyl)silane</pre>	80
10	<pre>(2-Chlorophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	100
	<pre>(4-Bromophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	90
15	<pre>[bis(2-Chlorophenyl)](lH-imidazol- l-ylmethyl)methylsilane</pre>	100
	<pre>[bis(4-Bromophenyl)](lH-imidazol-l- ylmethyl)methylsilane</pre>	50
•	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane, 1:1 complex with cuprous chloride</pre>	100
20	(2-Chlorophenyl)(4-chlorophenyl)(1H- imidazol-1-ylmethyl)methylsilane	80
	AB = Phytotoxic burn. 8Compound applied at a concentration	of 400 ppm.

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume. and then suspended at a concentration of 80 ppm in 5 purified water containing 250 ppm of the surfactant TREM 014 (polyhydric alcohol esters). This suspension was sprayed to the point of run-off on bean seedlings. The following day, the plants were inoculated with a spore suspension of the fungus Uromyces phase-10 oli, causal agent of bean rust, and incubated in a saturated humidity chamber at 20° for 24 hours and then in a greenhouse for 7 days. Disease ratings were then made. Percent disease control is shown in the following table. Treated plants had few or no rust 15 pustules in contrast to untreated plants which were covered with rust pustules. Phytotoxicity in the form of growth reduction was observed in association with disease control for some treated plants.

20	•	Table 7
20		Tante /

•	Compound	% Control Bean Rust
	(1,1'-Biphenyl-4-yl)dimethyl(lH- l,2,4-triazol-1-ylmethyl)silane	100
25	<pre>(2,4-Dichlorophenyl)dimethyl(1H- l,2,4-triazol-l-ylmethyl)silane</pre>	30G <sup>A</sup>
	<pre>bis(4-Chlorophenyl)(methyl)(lH-     1,2,4-triazol-l-ylmethyl)silane</pre>	100G
30	<pre>(4-Chlorophenyl)methyl(phenyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	988
	<pre>(4-Fluorophenyl)methyl(phenyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100 <sup>B</sup>
	<pre>bis(4-Fluorophenyl)(methyl)(lH-     1,2,4-triazol-l-ylmethyl)silane</pre>	988
35	<pre>(1,1'-Biphenyl-4-yl)dimethyl(lH- imidazol-l-ylmethyl)silane</pre>	100

0068813

### 150

### Table 7 (continued)

## Compound

% Control Bean Rust

(2,4-Dichlorophenyl)dimethyl(1Himidazol-1-ylmethyl)silane

83

 $^{\rm AG}$  = growth reduction.  $^{\rm B}$  compound applied at a concentration of 16 ppm.

10

5

15

20

25

30

35

Compounds of this invention were dissolved in acetone in an amount equal to 5% of the final volume and then suspended at a concentration of 100 ppm in 5 purified water containing 700 ppm of the surfactant TREM 014 (polyhydric alcohol esters). Canned peach halves were dipped in this suspension for three minutes and then placed to air dry in sterile containers. Upon drying, the peach halves were inocu-10 lated with two pieces of Monilinia fructicola mycelium, causal agent of stone fruit brown rot, and incubated in the sterile containers for five days. At that time the radii of the colonies' growth were measured on each peach. Colonies on treated peaches 15 did not grow or grew only a few milliliters in diameter while those growing on untreated peaches covered the entire surface of the peach. Percent disease contol (percent growth inhibition of colonies on treated peaches as compared to that of colonies on untreated peaches) is expressed in the table below. 20

25	Compound	% Control Brown Rot
	(Oimethyl)phenyl(1,2,4-triazol-1-ylmethyl)silane	89
30	(Butyl)dimethyl(1H-1,2,4-triazol-1-ylmethyl)silane	95
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100
•	<pre>Butyl(4-chlorophenyl)methyl(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	98
35	Dimethyl(4-methoxyphenyl)(1H-1,2,4- triazol-1-ylmethyl)silane	97

Table 8 (continued)

	Compound	% Control Brown Rot
5	<pre>(2,4-Dichlorophenyl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100
	<pre>bis(4-Chlorophenyl)(methyl)(lH-     1,2,4-triazol-l-ylmethyl)silane</pre>	95
10	<pre>(1,1'-8iphenyl-4-yl)dimethyl(4H- 1,2,4-triazol-4-ylmethyl)silane</pre>	96
	<pre>bis(4-Fluorophenyl)(methyl)(lH- l,2,4-triazol-1-ylmethyl)silane</pre>	100
1 =	Butyl(2,4-dichlorophenyl)methyl(1H- 1,2,4-triazol-l-ylmethyl)silane	98
15	(4-Chlorophenyl)methyl(phenyl)(1H- 1,2,4-triazol-1-ylmethyl)silane	70
	(4-Fluorophenyl)methyl(phenyl)(lH- 1,2,4-triazol-l-ylmethyl)silane	90
20	<pre>Butyl(4-fluorophenyl)methyl(1H-1,2,4- triazol-l-ylmethyl)silane</pre>	100
	<pre>Dibutyl(methyl)(lH-1,2,4-triazol-l- ylmethyl)silane</pre>	81
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	83
25	<pre>8utyl(4-chlorophenyl)(lH-imidazol- l-ylmethyl)methylsilane</pre>	45
	<pre>(lH-Imidazol-l-ylmethyl)dimethyl- (4-phenoxyphenyl)silane</pre>	80
30	<pre>(2,4-Dichlorophenyl)dimethyl(lH- imidazol-l-ylmethyl)silane</pre>	100
	<pre>Diphenyl(lH-imidazol-l-ylmethyl)-   methylsilane</pre>	76
76	<pre>(4-Chlorophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	45
35	<pre>(4-Fluorophenyl)(lH-imidazol-l-yl- methyl)methyl(phenyl)silane</pre>	65

### 153

### Example 76

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume and then suspended at a concentration of 100 ppm in purified water containing 250 ppm of the surfactant TREM 014 (polyhydric alcohol esters). This suspension was sprayed to the point of run-off on rice seedlings. The following day, the plants were inoculated with a mixture of bran and the mycelium of Rhizoctonia solani, causal agent of sheath blight of rice, and incubated in a growth room for 7 days. Disease ratings were then made. Percent disease control is shown in the following table. Treated plants had little sheath blight in contrast to untreated plants which were covered with sheath blight.

20	Compound		Control of Sheath Bli	
	<pre>(1,1'-8iphenyl-4-yl)dimethyl- (1H-1,2,4-triazol-l-ylmethyl)- silane</pre>		40	
25	(3,4-Dichlorophenyl)dimethyl(1H- 1,2,4-triazol-1-ylmethyl)silane	<b>;</b>	_ 80	
	<pre>bis(4-Fluorophenyl)(methyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	<b>:</b>	80 .	
	<pre>[4-(1,1-Dimethylethyl)phenyl]di- methyl(lH-1,2,4-triazol-1-yl- methyl)silane</pre>		90	
	Buty1(2,4-dichlorophenyl)methy1(1 1,2,4-triazol-1-ylmethyl)silane		50	
	(4-Chlorophenyl)methyl(phenyl)(lh l,2,4-triazol-l-ylmethyl)silane		90	
35	(4-Fluorophenyl)methyl(phenyl)(ll- 1,2,4-triazol-l-ylmethyl)silane		80	

# 154 Table 9 (continued)

	<u>Compound</u>		Control of Sheath Blight
5	<pre>Butyl(methyl)phenyl(lH-1,2,4-tria l-ylmethyl)silane</pre>	zol-	90
	(1,1'-Biphenyl-4-yl)butyl(methyl)- (1H-1,2,4-triazol-1-ylmethyl)si		80
10	<pre>Butyl(4-fluorophenyl)methyl(lH-l,:     triazol-l-ylmethyl)silane</pre>	2,4-	80
	<pre>bis(1,1'-Biphenyl-4-yl)(methyl)(18 1,2,4-triazol-1-ylmethyl)silane</pre>	H <b>-</b>	90
15	<pre>[bis(4-Methoxyphenyl)]methyl(lH-l triazol-l-ylmethyl)silane</pre>	, 2 , 4-	80
15	2-Chlorophenyl(methyl)phenyl(1H-l triazol-l-ylmethyl)silane	, 2 , 4-	<b>-</b> 90
	4-Bromophenyl(methyl)phenyl(lH-1, triazol-1-ylmethyl)silane	2,4-	90
20	<pre>[bis(2-Chlorophenyl)]methyl(1H-1,2 triazol-1-ylmethyl)silane</pre>	2,4-	60
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(1H-1   triazol-1-ylmethyl)silane, 1:1 o   plex with cuprous chloride</pre>		90
25	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1; triazol-1-ylmethyl)silane, l:l o plex with zinc (II) chloride</pre>		90
	2-Chlorophenyl(4-chlorophenyl)meth (1H-1,2,4-triazol-1-ylmethyl)si		70
30	<pre>[bis(2-Fluorophenyl)]methyl(lH- l,2,4-triazol-l-ylmethyl)silane l:l complex with cuprous chloric</pre>	, de	90
	(1H-Imidazol-l-ylmethyl)dimethyl- (4-phenoxyphenyl)silane		70
	<pre>bis(4-Fluorophenyl)(lH-imidazol-l- ylmethyl)methylsilane</pre>	•	90

# 

# Table 9 (continued)

	Compound		Control of Sheath Blight
5	(lH-Imidazol-l-ylmethyl)dimethyl- (2-trifluoromethylphenyl)silane		80
	<pre>Butyl(2,4-dichlorophenyl)(lH-imid zol-l-ylmethyl)methylsilane</pre>	ia-	90
10	<pre>bis(2,4-Dichlorophenyl)(lH-imidaz l-ylmethyl)methylsilane</pre>	ol-	80
	(4-Fluorophenyl)(1H-imidazol-l-yl methyl)methyl(phenyl)silane		90
	(1H-Imidazol-l-ylmethyl)(2-methox phenyl)dimethylsilane	xy <b>–</b>	90
15	[4-(4-Chlorophenoxy)phenyl]dimeth (lH-imidazol-l-ylmethyl)silane	yl-	70
	<pre>Butyl(lH-imidazol-l-ylmethyl)- methyl(phenyl)silane</pre>		80
20	(1,1'-8iphenyl-4-yl)butyl(lH-imid zol-1-ylmethyl)methylsilane	la-	90
	Butyl(4-fluorophenyl)(lH-imidazol l-ylmethyl)methylsilane		80
	<pre>(1,1'-8iphenyl-2-yl)dimethyl(lH- imidazol-l-ylmethyl)silane</pre>		90 <sup>.</sup>
25	<pre>(1,1'-8iphenyl-3-yl)dimethyl(lH- imidazol-l-ylmethyl)silane</pre>		90
	<pre>[bis(2-Chlorophenyl)](lH-imidazol l-ylmethyl)methylsilane</pre>		40
30	<pre>(1,1'-Biphenyl-4-yl)dimethyl(lH- imidazol-l-ylmethyl)silane, 1:l complex with cuprous chloride</pre>		50
	(2-Chlorophenyl)(dimethyl)(lH-imidazol-l-ylmethyl)silane	. <b>-</b>	90

#### 156

### Example 77

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume and then suspended at a concentration of 100 ppm in purified water containing 250 ppm of the surfactant TREM 014 (polyhydric alcohol esters). These suspensions were sprayed to the point of run-off on rice seedlings. The following day, the plants were inoculated with a spore suspension of <a href="Pyricularia oryzae">Pyricularia oryzae</a>, causal agent of rice blast, and incubated in a saturated humidity chamber at 28°C for 24 hours and then in a growth room for an additional 7 days, when disease ratings were made. Percent disease control is shown in the following table. Treated plants had no or few lesions while the untreated plants had numerous lesions on each leaf.

20	<u>Compound</u>	% Control of Rice Blast
	Dimethyl(1-naphthalenyl)(1H-1,2,4-triazol-1-ylmethyl)silane	70
25	<pre>bis(4-Chlorophenyl)(methyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	90
	<pre>bis(4-Fluorophenyl)(methyl)(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	100
30	<pre>[4-(1,1-Dimethylethyl)phenyl]di- methyl(lH-1,2,4-triazol-1-yl- methyl)silane</pre>	90
	(4-Chlorophenyl)methyl(phenyl)(1H- 1,2,4-triazol-l-ylmethyl)silane	100
	<pre>Butyl(methyl)phenyl(lH-1,2,4-triazo l-ylmethyl)silane</pre>	90
35	(2-Chlorophenyl)dimethyl(1H-1,2,4- triazol-1-ylmethyl)silane	100

# Table 10 (continued)

	Compound	% Control of Rice Blast
5	(1,1'-Biphenyl-4-yl)butyl(methyl)- (1H-1,2,4-triazol-1-ylmethyl)sila	ine 100
	<pre>Butyl(4-fluorophenyl)methyl(1H-1,2,     triazol-l-ylmethyl)silane</pre>	100
10	Dibutyl(methyl)(lH-1,2,4-triazol-1-ylmethyl)silane	80
	bis(1,1'-8iphenyl-4-y1)(methyl)(1H-1,2,4-triazol-1-ylmethyl)silane	100
	(1,1'-Biphenyl-2-yl)dimethyl(1H-1,2 triazol-1-ylmethyl)silane	2,4 <b>-</b> 90
15	2-Chlorophenyl(methyl)phenyl(1H-1,2 triazol-1-ylmethyl)silane	2,4-
	4-Bromophenyl(methyl)phenyl(1H-1,2, triazol-1-ylmethyl)silane	,4 <b>-</b> 80
20	<pre>[bis(2-Chlorophenyl)]methyl(lH-1,2, triazol-1-ylmethyl)silane</pre>	,4 <b>-</b> 90
	Oimethyl(4-methylsulfonylphenyl)(18 1,2,4-triazol-1-ylmethyl)silane	1 <b>-</b> 70
	[bis(4-Bromophenyl)]methyl(1H-1,2,4 triazol-1-ylmethyl)silane	4 <b>-</b> . 90
25	(1,1'-Biphenyl-4-yl)dimethyl(1H-1,2 triazol-1-ylmethyl)silane, 4-dode benzenesulfonic acid salt	2,4- ecyl- 80
30	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1, triazol-1-ylmethyl)silane, 1:1 complex with cuprous chloride</pre>	2,4- om- 100
	<pre>(1,1'-8iphenyl-4-y1)dimethyl(1H-1, triazol-1-ylmethyl)silane, 1:1 c plex_with zinc (II) chloride</pre>	2,4- om- 100
35	<pre>[bis(2-Fluorophenyl)]methyl(lH- l,2,4-triazol-l-ylmethyl)silane, l:l complex with cuprous chlorid</pre>	, . e 90

# 

# Table 10 (continued)

	Compound	% Control of Rice Blast
5	<pre>[bis(2-Fluorophenyl)]methyl(lH- 1,2,4-triazol-l-ylmethyl)silane, 2:1 complex with cupric chloride</pre>	100
	(lH-Imidazol-l-ylmethyl)dimethyl- (4-phenoxyphenyl)silane	70
10	[4-(1,1-Oimethylethyl)phenyl](1H-imidazol-1-ylmethyl)dimethylsilar	ne 80
	(4-Fluorophenyl)(lH-imidazol-l-yl-methyl)methyl(phenyl)silane	100
15	[4-(4-Chlorophenoxy)phenyl]dimethyl (lH-imidazol-l-ylmethyl)silane	- 100
	<pre>Butyl(lH-imidazol-l-ylmethyl)-   methyl(phenyl)silane</pre>	90
	(1,1'-Biphenyl-4-yl)butyl(lH-imida- zol-1-ylmethyl)methylsilane	90
20	Butyl(4-fluorophenyl)(lH-imidazol- l-ylmethyl)methylsilane	100
	<pre>(1,1'-8iphenyl-2-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	90
25	<pre>(1,1'-Biphenyl-3-yl)dimethyl(lH- imidazol-l-ylmethyl)silane</pre>	80
	<pre>[bis(2-Chlorophenyl)](lH-imidazol- l-ylmethyl)methylsilane</pre>	90
	Dimethyl(lH-imidazol-l-ylmethyl)- (4-methylsulfonylphenyl)silane	100
30	[bis(4-8romophenyl)](1H-imidazol-l-ylmethyl)methylsilane	80

Compounds of this invention were dissolved in acetone in an amount equal to 6% of the final volume and then suspended at a concentration of 100 ppm in purified water containing 250 ppm of the surfactant TREM 014 (polyhydric alcohol esters). These suspensions were sprayed to the point of run-off-on-tomato seedlings. The following day, the plants were inoculated with a spore suspension of <a href="Phytophthora infes-tans">Phytophthora infes-tans</a>, causal agent of tomato late blight, and incubated in a saturated humidity chamber at 20°C for 24 hours and then in a growth room for an additional 7 days, when disease ratings were made. Percent disease control is shown in the following table. Treated plants had no or few lesions while the untreated plants had numerous lesions on each leaf.

20	Compound	% Co Tomato	ntrol Late	
	Dimethyl(4-phenoxyphenyl)(1H-1,2,4-triazol-1-ylmethyl)silane		50	
25	[4-(4-Chlorophenoxy)phenyl]dimethyl (1H-1,2,4-triazol-l-ylmethyl)sila		50	
	<pre>(1,1'-Biphenyl-2-yl)dimethyl(lH-1,2 triazol-1-ylmethyl)silane</pre>	,4-	50	
30	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1,2 triazol-1-ylmethyl)silane, 4-dode benzenesulfonic acid salt</pre>		60	
	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH-1,2 triazol-l-ylmethyl)silane, 1:1 co plex with cuprous chloride</pre>	m-	.00	
35	(1,1'-Biphenyl-4-yl)dimethyl(1H-1,2 triazol-1-ylmethyl)silane, 1:1 co plex with zinc (II) chloride		90	

# 

# Table 11 (continued)

	Compound	% Control of Tomato Late Blight
5	<pre>[bis(2-Fluorophenyl)]methyl(lH- l,2,4-triazol-l-ylmethyl)silane, 2:1 complex with cupric chloride</pre>	40
	(4-Bromophenyl)(lH-imidazol-l-yl-methyl)dimethylsilane	30
10	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	50
	(lH-Imidazol-l-ylmethyl)dimethyl- (4-phenoxyphenyl)silane	80
15	Dimethyl(lH-imidazol-l-ylmethyl)- (3-trifluoromethylphenyl)silane	70
	(2,6-Dimethoxyphenyl)(dimethyl)(1H-imidazol-l-ylmethyl)silane	<b>-</b> 50
	[bis(2-Chlorophenyl)](lH-imidazol- l-ylmethyl)methylsilane	60
20		

Compounds of this invention were incorporated into 45°C standard strength V-8 agar at a concentration of 200.0 ppm. The amended media were then dispensed into petri dishes and allowed to solidify. Plugs approximately 4 mm² from agar cultures of 5 Phytophthora species: Phytophthora cinnamomi, P. cactorum, P. infestans, P. palmivora, and P. parasitica var. nicotianae were placed on the media and incubated at 22°C for 6 days. Colonies whose radial growth extended 1 mm or less were considered to be controlled by a compound when compared to colonies whose radial growth extended 15 mm or more when growing on unamended media. The number of Phytophthora species controlled by certain compounds of this invention are listed in the table below.

20	: <u>Compound</u>	#				thora in v	spec itro	ies
	(Butyl)dimethyl(1H-1,2,4-trylmethyl)silane	iaz	zo1.	-1-	•	1		
25	(3,4-Dichlorophenyl)dimethyl			9		2		
	(1,1'-8iphenyl-4-yl)dimethy imidazol-1-ylmethyl)silan		LH-			3		
30	(lH-Imidazol-l-ylmethyl)dim (4-phenoxyphenyl)silane	eti	nyl.	-		4		
	(2,4-Dichlorophenyl)dimethy imidazol-l-ylmethyl)silan		LH-	•		5		
	Oiphenyl(lH-imidazol-l-ylme methylsilane	thy	y1)·	-		2		
35	(4-Fluorophenyl)(lH-imidazo methyl)methyl(phenyl)sila		l-y	1-		2	٠	

Compounds of this invention were incorporated into a proprietary formulation and used to coat cotton seeds at a rate of 2 gm/kg seed. After being thoroughly coated, the seeds were allowed to air dry at room temperature. The cotton seeds were then planted into soil amended with the fungus Pythium aphanader—matum, sand, and corn meal at a rate sufficient to kill most untreated seeds. The seeds were held at room temperature for 1 week, after which time disease ratings were made. Percent disease control is shown in the following table. Most or all seeds from treatments germinated and produced vigorous seedlings in contrast to untreated seeds which either did not germinate or produced damped off or weak seedlings.

20	Compound	% Control of Pythium on Cotton
	Ethyldimethyl(1H-1,2,4-triazol-1-ylmethyl)silane	48
25	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH- l,2,4-triazol-l-ylmethyl)silane</pre>	12
	(4-Chlorophenyl)dimethyl(lH-1,2,4-triazol-l-ylmethyl)silane	53A
	<pre>Dimethyl(4-phenoxyphenyl)(1H-1,2,4- triazol-l-ylmethyl)silane</pre>	- 18 <sup>A</sup>
30	<pre>(1,1'-Biphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane</pre>	18
	(4-Chlorophenyl)(lH-imidazol-l- ylmethyl)dimethylsilane	18A
	(3,4-Dichlorophenyl)(1H-imidazol- l-ylmethyl)dimethylsilane	15 <sup>A</sup>
35	Acontrol at a rate of 0.5 gm/kg see	ed.

Compounds of this invention were incorporated into a proprietary formulation and used to coat corn seeds at a rate of 2 gm/kg seed. After being thoroughly coated, the seeds were allowed to air dry at room temperature. The seeds were then planted into soil amended with a mixture of the fungus <a href="Pythium aphanadermatum">Pythium aphanadermatum</a>, sand, and corn meal at a rate sufficient to kill most untreated seeds. The seeds were held at 49°F for 2 weeks and then at 70°F for 1 additional week. After this time disease ratings were made. Percent disease control is shown in the following table. Most or all seeds from treatments germinated and produced vigorous seedlings in contrast to untreated seeds which either did not germinate or produced damped off or weak seedlings.

20	Compound	% Control of Pythium on Corn
	Ethyldimethyl(lH-1,2,4-triazol-1-ylmethyl)silane	13
25	<pre>(1,1'-8iphenyl-4-yl)dimethyl(lH- 1,2,4-triazol-1-ylmethyl)silane</pre>	. 30
	(4-Chlorophenyl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)silane	8
70	<pre>Dimethyl(l-naphthalenyl)(lH-1,2,4- triazol-l-ylmethyl)silane</pre>	30
30	(3,4-Dichlorophenyl)dimethyl(lH- 1,2,4-triazol-l-ylmethyl)silane	43
	<pre>Ethyl(lH-imidazol-l-ylmethyl)-   dimethylsilane</pre>	70
35	<pre>(lH-Imidazol-l-ylmethyl)dimethyl- (4-methylphenyl)silane</pre>	30

# 

# Table 14 (continued)

	Compound	% Control of Pythium on Corn
5	(1,1'-8iphenyl-4-yl)dimethyl(lH- imidazol-1-ylmethyl)silane	32
	(4-Chlcrophenyl)(lH-imidazol-l- ylmethyl)dimethylsilane	25
10	(lH-Imidazol-l-ylmethyl)dimethyl- (l-naphthalenyl)silane	27
	(3,4-Dichlorophenyl)(lH-imidazol- l-ylmethyl)dimethylsilane	30
	(lH-Imidazol-l-ylmethyl)dimethyl- (4-phenoxyphenyl)silane	5
15	Dimethyl(4-fluorophenyl)(lH-imi- dazol-l-ylmethyl)silane	15.

Claims:

### 1. A compound of the formula:

wherein

 $\mathbb{Q}_1$  and  $\mathbb{Q}_2$  are independently H or  $\mathrm{CH}_3$ ; n is 1;

R<sub>1</sub> is C<sub>2</sub>-C<sub>18</sub> alkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, naphthyl, or

where

 $R_4$  and  $R_5$  are independently -H; halogen;  $-0\text{CH}_3$ ;  $-0\text{CF}_3$ ;  $-\text{SCH}_3$ ;  $-\text{SO}_2\text{CH}_3$ ; phenyl; phenyl substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or -CF $_3$ ; phenoxy; phenoxy substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or -CF $_3$ ; -CF $_3$ ;  $C_1$ - $C_4$  alkyl; or cyclohexyl;

 $\rm R_2$  and  $\rm R_3$  are independently  $\rm C_1-\rm C_6$  alkyl,  $\rm C_3-\rm C_6$  cycloalkyl,  $\rm OR_6,$  or

where  $R_6$  is H or  $C_1$ - $C_4$  alkyl, or one  $R_6$  group

may be

with the proviso that both  $R_2$  and  $R_3$  may not be 0H; and  $R_2$  and  $R_3$  together may be a 1,2- or 1,3- or 1,4-glycol bridge or a 1,4 unsaturated glycol bridge which may optionally be substituted by up to four alkyl groups  $R_7$ - $R_{10}$  that have a total of up to four carbon atoms, viz.

$$R_7^{-R_{10}}$$
 or  $R_7^{-R_{10}}$  or  $R_7^{-R_{10}}$  or  $R_7^{-R_{10}}$ 

and salts thereof with protic acids and complexes with metal ions.

### 2. A compound of the formula:

wherein

 $\mathbf{Q}_1,\ \mathbf{Q}_2$  and  $\mathbf{Q}_3$  are independently H or  $\mathrm{CH}_3;$  n is 1;

R'<sub>1</sub> is C<sub>6</sub>-C<sub>18</sub> alkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, naphthyl or

where

R<sub>4</sub> and R<sub>5</sub> are independently -H; halogen; -OCH<sub>3</sub>; -OCF<sub>3</sub>; -SCH<sub>3</sub>; -SO<sub>2</sub>CH<sub>3</sub>; phenyl; phenyl substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or - $CF_3$ ; phenoxy; phenoxy substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or - $CF_3$ ; - $CF_3$ ;  $C_1$ - $C_4$  alkyl; or cyclohexyl; with the proviso that for compounds of Formula II, both  $R_4$  and  $R_5$  may not simultaneously be H; and  $R_2$  and  $R_3$  are independently  $C_1$ - $C_6$  alkyl,  $C_3$ - $C_6$  cycloalkyl,  $OR_6$ , or

where  $R_4$  and  $R_5$  are as defined above except that said proviso does not apply, and  $R_6$  is H or  $C_1-C_4$  alkyl, or one  $R_6$  group may be

with the proviso that both  $R_2$  and  $R_3$  may not be 0H; and  $R_2$  and  $R_3$  together may be a 1,2- or 1,3- or 1,4-glycol bridge or a 1,4 unsaturated glycol bridge which may optionally be substituted by up to four alkyl groups  $R_7$ - $R_{10}$  that have a total of up to four carbon atoms, viz.

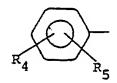


01

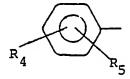


and salts thereof with protic acids and complexes with metal ions.

- 3. A compound of claim 1 or 2 wherein  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$  are H.
- 4. A compound of claim 3 wherein  $R_1$  or  $R_1^*$  is

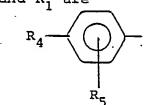


 $R_2$  is  $C_1-C_4$  alkyl or

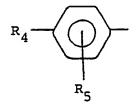


and  $R_3$  is  $C_1-C_4$  alkyl.

5. A compound of claim 4 wherein  $R_1$  and  $R_1^*$  are



where  $R_4$  is H, F, Cl, Br or phenyl, and  $R_5$  is H, F, Cl or Br; and  $R_2$  is

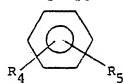


or  $C_1-C_4$  alkyl; and  $R_3$  is  $C_1-C_4$  alkyl.

- 6. The compound of Claim 1 which is (1,1'-bi-phenyl-4-yl)dimethyl(lH-1,2,4-triazol-1-ylmethyl)-silane.
- 7. The compound of Claim 1 which is bis(4-chlorophenyl)methyl(1H-1,2,4-triazol-1-ylmethyl)-silane.
- 8. The compound of Claim 1 which is [bis(4-fluorophenyl)]methyl(1H-1,2,4-triazol-1-ylmethyl)-silane.
- 9. The compound of Claim 1 which is 4-fluorophenyl(methyl)phenyl(lH-1,2,4-triazol-1-ylmethyl)silane.
- 10. The compound of claim 2 which is (2,4-di-chlorophenyl)dimethyl(lH-imidazol-l-ylmethyl)silane.
  - 11. A compound of claim 1 wherein:

 $Q_1$  and  $Q_2$  are H;  $R_1$  is  $C_2$ - $C_{18}$  alkyl,  $C_3$ - $C_6$  cycloalkyl,

naphthyl, or



where  $R_4$  and  $R_5$  are independently -H, halogen, phenyl, -OCH<sub>3</sub>, -SCH<sub>3</sub>, phenoxy, -CF<sub>3</sub> or  $C_1$ - $C_4$  alkyl; and  $R_1$  and  $R_3$  are independently  $C_1$ - $C_6$  alkyl,  $C_3$ - $C_6$  cycloalkyl, or  $OR_6$ , where  $R_6$  is H or  $C_1$ - $C_4$  alkyl.

12. A compound of claim 2 wherein

Q<sub>1</sub>, Q<sub>2</sub> and Q<sub>3</sub> are H; R'<sub>1</sub> is

where  $R_4$  and  $R_5$  are as defined in claim 11 but are not both H; and

 $\rm R_2$  and  $\rm R_3$  are independently  $\rm C_1-\rm C_4$  alkyl or  $\rm OR_6$  , where  $\rm R_6$  is H or  $\rm C_1-\rm C_4$  alkyl.

13. A composition for controlling fungus

diseases comprising an effective amount of a fungicidal compound and at least one of the following: surfactant, solid or liquid inert diluent, characterised in

that said fungicidal compound comprises a compound of any of claims 1 to 12.

14. A method for controlling fungus diseases by applying to the locus to be protected an effective amount of a fungicidal compound, characterised in

that said fungicidal compound comprises a compound of any of claims 1 to 12.

15. A method for controlling fungus diseases by applying to the locus to be protected an effective amount of a fungicidal compound, characterised in

that said fungicidal comprises a compound of the formula:

wherein

 $\mathbf{Q}_{1}$  ,  $\mathbf{Q}_{2}$  ,  $\mathbf{Q}_{3}$  , n,  $\mathbf{R}_{2}$  ,  $\mathbf{R}_{3}$  , and  $\mathbf{R}_{6}$  are as defined in claim 2, and

R'<sub>1</sub> is C<sub>2</sub>-C<sub>18</sub> alkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, naphthyl or

where

 $R_4$  and  $R_5$  are independently -H; halogen;  $-0\text{CH}_3$ ;  $-0\text{CF}_3$ ;  $-\text{SCH}_3$ ;  $-\text{SO}_2\text{CH}_3$ ; phenyl; phenyl substituted with halogen and/or  $C_1-C_4$  alkyl and/or  $-\text{CF}_3$ ; phenoxy; phenoxy substituted with halogen and/or

 $C_1-C_4$  alkyl and/or  $-CF_3$ ;  $-CF_3$ ;  $C_1-C_4$  alkyl; or cyclohexyl; or a salt thereof with a protic acid or a complex thereof with a metal ion.

16. A process for preparing a compound of claim 1 or 2 which comprises reacting a silane derivative of formula

$$R_1 = \frac{R_2}{S_1 - CH_2 Y}$$
 or  $R_1 = \frac{R_2}{R_3}$ 

wherein  $R_1$ ,  $R_1$ ,  $R_2$  and  $R_3$  are as defined in claims 1 and 2 and Y is chlorine, bromine, iodine or arylsulfonyloxy, with a 1,2,4-triazole or imidazole of formula

wherein  $Q_1$  and  $Q_2$  are independently H or  $CH_3$  and X is H, CH or  $CCH_3$ , or with an alkali metal salt thereof.

17. A process for preparing a compound of claims 1 or 2 wherein  $R_2$  and/or  $R_3$  is  $OR_6$  which comprises reacting a corresponding compound of formula

wherein  $R_2^*$  is halogen or  $R_2$  and  $R_3^*$  is halogen or  $R_3$ , at least one of  $R_2$  and  $R_3$  being halogen, and Y is as defined in claim 15, with a triazole or imidazole sodium salt of formula

wherein X is N, CH or  $CCH_3$ , and reacting the intermediate so obtained with  $R_6$  OH to obtain a compound

of claim 1 or 2 wherein  $R_2$  and/or  $R_3$  is  $R_6^0$ ;

 $\rm R_1$  having a value as defined for  $\rm R_1^1$  in claim 2 when X is CH or  $\rm CCH_3$  .

18. A process for preparing a compound of claim 1 which comprises reacting 1) an intermediate selected from the group

 $R_3$   $R_2$   $R_3$   $R_2$   $R_2$   $R_3$   $R_2$   $R_3$   $R_3$   $R_2$   $R_3$   $R_3$ 

in a suitable solvent with R<sub>1</sub>M where M is Na, Li or MgX where X is 8r, Cl, I, at a temperature of from -80° to 40°C to form a chloromethylsilane; and 2) reacting the chloromethylsilane with 1,2,4-triazole, its 3-methyl or 3,5-dimethyl derivative, or their alkali metal salts in polar aprotic solvents, ethers or ketones at 0° to 200°C; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> being as defined in claim 1. 19. A process for preparing a compound of Claim 1 which comprises 1) reacting

with  $R_6^{\rm OH}$  in a suitable solvent with a suitable base at a temperature of 0°-100°C to form an alkoxy or dialkoxy chloromethyIsilane; and 2) reacting the chloromethyIsilanes with 1,2,4-triazole, its 3-methyl or 3,5-dimethyl derivative, or their alkali metal salts in polar aprotic solvents, ethers or ketones at 0° to 200°C;  $R_1$ ,  $R_2$  and  $R_6$  being as defined in claim 1.

20. A process for preparing a compound of claim 2 which comprises reacting 1) an intermediate selected from the group

in a suitable solvent with R<sub>1</sub>M where M is Na,
Li or MgX where X is Br, Cl, I, at a temperature
of from -80° to 40°C to form a chloromethylsilane; and 2) reacting the chloromethylsilane
with imidazole, its 2-methyl, 2,4-dimethyl,
4,5-dimethyl, and 2,4,5-trimethyl derivatives,
or their alkali metal salts in polar aprotic
solvents, ethers or ketones at 0° to 200°C;
R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> being as defined in claim 2.
21. A process for preparing a compound of claim
2 which comprises 1) reacting

with R $_6$ OH in a suitable solvent with a suitable base at a temperature of O° to 100°C to form an alkoxy or dialkoxy chloromethylsilane; and 2) reacting the chloromethylsilane with imidazole, its 2-methyl, 2,4-methyl, 4,5-methyl, and 2,4,5-trimethyl derivatives, or their alkali metal salts in polar aprotic solvents, ethers or ketones at O° to 200°C;  $R_1^4$ ,  $R_2$  and  $R_6$  being as defined in claim 2.

Claims: AT

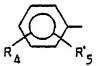
1. A process for the preparation of a compound of the formula:

I

wherein

 $\mathbb{Q}_1$  and  $\mathbb{Q}_2$  are independently H or  $\mathbb{CH}_3$ ; n is 1;

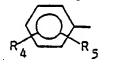
R<sub>1</sub> is C<sub>2</sub>-C<sub>18</sub> alkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, naphthyl, or



where

 $R_{4}$  and  $R_{5}$  are independently -H; halogen;  $-0\text{CH}_{3}$ ;  $-0\text{CF}_{3}$ ;  $-\text{SCH}_{3}$ ;  $-\text{SO}_{2}\text{CH}_{3}$ ; phenyl; phenyl substituted with halogen and/or  $C_{1}^{-C_{4}}$  alkyl and/or  $-\text{CF}_{3}$ ; phenoxy; phenoxy substituted with halogen and/or  $C_{1}^{-C_{4}}$  alkyl and/or  $-\text{CF}_{3}$ ;  $-\text{CF}_{3}$ ;  $C_{1}^{-C_{4}}$  alkyl; or cyclohexyl;

 $R_2$  and  $R_3$  are independently  $C_1$ - $C_6$  alkyl,  $C_3$ - $C_6$  cycloalkyl,  $OR_6$ , or



where  $R_6$  is H or  $C_1$ - $C_4$  alkyl, or one  $R_6$  group may be

with the proviso that both  $R_2$  and  $R_3$  may not be OH; and  $R_2$  and  $R_3$  together may be a 1,2- or 1,3- or 1,4-glycol bridge or a 1,4 unsaturated glycol bridge which may optionally be substituted by up to four alkyl groups  $R_7$ - $R_{10}$  that have a total of up to four carbon atoms,

and salts thereof with protic acids and complexes with metal ions, which comprises (a) reaction of a silane derivative of formula

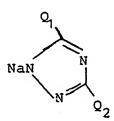
# -3- AT

wherein  $R_1$ ,  $R_2$  and  $R_3$  are as defined above and Y is chlorine, bromine or arylsulfonyloxy, with a 1,2,4-triazole of formula

wherein  $Q_1$  and  $Q_2$  are as defined above or with an alkali metal salt thereof; or

(b) reacting a corresponding compound of formula

wherein  $R_1$  and Y are as defined above,  $R_2'$  is halogen or  $R_2$  and  $R_3$  is halogen or  $R_3$ , at least one of  $R_2'$  and  $R_3'$  being halogen, with a triazole sodium salt of formula



wherein  $Q_1$  and  $Q_2$  are as defined above, and reacting the intermediate so obtained with  $R_6$ OH to obtain a product of formula I wherein  $R_2$  and/or  $R_3$  is  $R_6$ O.

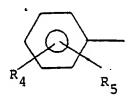
2. A process for the preparation of a compound of formula I as defined in claim 1, which comprises reacting 1) an intermediate selected from the group

$$R_3$$
  $R_2$   $R_2$   $R_2$   $R_2$   $R_2$   $R_2$   $R_3$   $R_2$   $R_3$   $R_3$ 

in a suitable solvent with R<sub>1</sub>M where M is Na, Li or MgX where X is Br, Cl, I, at a temperature of from -80°C to 40°C to form a chloromethylsilane; and 2) reacting the chloromethylsilane with 1,2,4-triazole, its 3-methyl or 3,5-dimethyl derivative, or their alkali metal salts in polar aprotic solvents, ethers or ketones at 0° to 200°C; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> being as defined in claim 1.

3. The process of claim 1 or claim 2 wherein:  $Q_1$  and  $Q_2$  are H;  $R_1$  is  $C_2$ - $C_{18}$  alkyl,  $C_3$ - $C_6$  cycloalkyl,

naphthyl, or



where  $R_4$  and  $R_5$  are independently -H, halogen, phenyl,-OCH<sub>3</sub>, -SCH<sub>3</sub>, phenoxy, -CF<sub>3</sub> or  $C_1$ - $C_4$  alkyl; and  $R_1$  and  $R_3$  are independently  $C_1$ - $C_6$  alkyl,  $C_3$ - $C_6$  cycloalkyl, or OR<sub>6</sub>, where  $R_6$  is H or  $C_1$ - $C_4$  alkyl.

4. A process for the preparation of a compound of the formula:

$$\begin{array}{c} R_2 - Si(CH_2) \\ R_3 \end{array} \qquad \begin{array}{c} Q_1 \\ N \\ Q_3 \end{array}$$

wherein

 $\mathbf{Q}_1$ ,  $\mathbf{Q}_2$  and  $\mathbf{Q}_3$  are independently H or  $\mathbf{CH}_3$ ; n is 1;

R'<sub>1</sub> is C<sub>6</sub>-C<sub>18</sub> alkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, naphthyl or

where

 $R_4$  and  $R_5$  are independently -H; halogen;  $-0\text{CH}_3$ ;  $-0\text{CF}_3$ ;  $-\text{SCH}_3$ ;  $-\text{SO}_2\text{CH}_3$ ; phenyl; phenyl substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or -CF $_3$ ; phenoxy; phenoxy substituted with halogen and/or  $C_1$ - $C_4$  alkyl and/or -CF $_3$ ; -CF $_3$ ;  $C_1$ - $C_4$  alkyl; or cyclohexyl; with the proviso that for compounds of Formula

II, both  $R_4$  and  $R_5$  may not simultaneously be H; and

 $\rm R_2$  and  $\rm R_3$  are independently  $\rm C_1\text{-}C_6$  alkyl,  $\rm C_3\text{-}C_6$  cycloalkyl,  $\rm OR_6,$  or

# -6-AT

where  $R_4$  and  $R_5$  are as defined above except that said proviso does not apply and  $R_6$  is H or  $C_1 - C_4$  alkyl, or one  $R_6$  group may be

with the proviso that both  $R_2$  and  $R_3$  may not be OH; and  $R_2$  and  $R_3$  together may be a 1,2- or 1,3- or 1,4-glycol bridge or a 1,4 unsaturated glycol bridge which may optionally be substituted by up to four alkyl groups  $R_7$ - $R_{10}$  that have a total of up to four carbon atoms, viz

and salts thereof with protic acids and complexes with metal ions, which comprises

(a) reacting a silane derivative of formula

wherein  $R_1'$ ,  $R_2$  and  $R_3$  are as defined above and Y is chlorine, bromine, iodine or arylsulfonyloxy, with an imidazole of formula

wherein  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$  are as defined above, or with an alkali metal salt thereof, or

(b) reacting a corresponding compound of formula

wherein  $R_1^i$  and Y are as defined above,  $R_2^i$  is halogen or  $R_2$ ,  $R_3^i$  is halogen or  $R_3$ , at least one of  $R_2^i$  and  $R_3^i$  being halogen, with an imidazole sodium salt of formula

wherein  $Q_1$  and  $Q_2$  are as defined above, and reacting the intermediate so obtained with  $R_6$ OH to obtain a compound of formula II wherein  $R_2$  and/or  $R_3$  is  $R_6$ O.

5. A process for the preparation of a compound of

formula II as defined in claim 4 which comprises reacting 1) an intermediate selected from the group

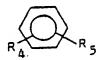
# -8- AT

 $\text{Cl}_3\text{SiCH}_2\text{Cl}, \text{Cl}_2\overset{\text{R}_3}{\text{SiCH}_2}\text{Cl} \text{ and } \text{Cl}-\overset{\text{R}_2}{\text{Si}-\text{CH}_2}\text{Cl}$ 

in a suitable solvent with R'M where M is Na, Li or MgX where X is Br, Cl, I, at a temperature of from -80°C to 40°C to form a chloromethyl-silane; and 2) reacting the chloromethylsilane with imidazole, its 2-methyl, 2,4-dimethyl, 4,5-dimethyl, and 2,4,5-trimethyl derivatives, or their alkali metal salts in polar aprotic solvents, ethers or ketones at 0° to 200°C; R'1, R2 and R3 being as defined in claim 2. The process of claims 4 or 5 wherein

 $\mathbf{Q}_1$ ,  $\mathbf{Q}_2$  and  $\mathbf{Q}_3$  are  $\mathbf{H}$ ;  $\mathbf{R}_1^\prime$  is

6.

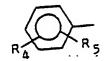


where  $R_4$  and  $R_5$  are as defined in claim 3 but are not both H; and

 $\rm R_2$  and  $\rm R_3$  are independently  $\rm C_1-\rm C_4$  alkylor  $\rm OR_6$ , where  $\rm R_6$  is H or  $\rm C_1-\rm C_4$  alkyl.

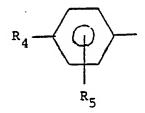
7. The process of any of claims 1-6 wherein  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$  are H,  $\mathbf{R}_1$  or  $\mathbf{R}_1'$  is

 $R_2$  is  $C_1-C_4$  alkyl or

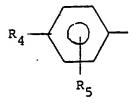


and  $R_3$  is  $C_1-C_4$  alkyl.

8. The process of claim 7 wherein R<sub>1</sub> and R<sub>2</sub> are



where  $R_4$  is H, F, Cl, Br or phenyl, and  $R_5$  is H, F, Cl or Br; and  $R_2$  is



or  $C_1-C_4$  alkyl; and  $R_3$  is  $C_1-C_4$  alkyl.

9. The process of claim 1 or 4 wherein the product is selected from:

(1,1'-bi-phenyl-4-yl)dimethyl(1H-1,2,4-triazol-1ylmethyl)-silane;

bis(4-chlorophenyl)methyl(1H-1,2,4-triazol-1ylmethyl)-silane;

# -10- AT

[bis(4-fluorophenyl)]methyl(1H-1,2,4-triazol1-ylmethyl)-silane;

4-fluorophenyl (methyl) phenyl (1H-1,2,4-triazol-1-ylmethyl) -silane; and

- (2,4-dichlorophenyl)dimethyl(1H-imidazol-l-ylmethyl)silane.
- 10. A method for controlling fungus diseases by applying to the locus to be protected an effective amount of a fungicidal compound, characterised in

that said fungicidal compound comprises a compound of formula I as defined in any of claims 1-3 or 7-9.

11. A method for controlling fungus diseases by applying to the locus to be protected an effective amount of a fungicidal compound, characterised in

that said fungicidal compound comprises a compound of formula II as defined in any of claims 4-9.

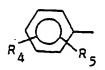
12. A method for controlling fungus diseases by applying to the locus to be protected an effective amount of a fungicidal compound, characterised in

that said fungicidal compound comprises a compound of formula :

wherein

 $\mathbf{Q}_{1}$  ,  $\mathbf{Q}_{2}$  ,  $\mathbf{Q}_{3}$  , n,  $\mathbf{R}_{2}$  ,  $\mathbf{R}_{3}$  and  $\mathbf{R}_{6}$  are as defined in claim 2, and

 $R_1'$  is  $C_2-C_{18}$  alkyl,  $C_3-C_6$  cycloalkyl, naphthyl or



where

R<sub>4</sub> and R<sub>5</sub> are independently -H; halogen;
-OCH<sub>3</sub>; -OCF<sub>3</sub>; -SCH<sub>3</sub>; -SO<sub>2</sub>CH<sub>3</sub>; phenyl;
phenyl substituted with halogen and/or
C<sub>1</sub>-C<sub>4</sub> alkyl and/or -CF<sub>3</sub>; phenoxy;
phenoxy substituted with halogen and/or
C<sub>1</sub>-C<sub>4</sub> alkyl and/or -CF<sub>3</sub>; -CF<sub>3</sub>;
C<sub>1</sub>-C<sub>4</sub> alkyl; or cyclohexyl; or a salt thereof with a protic acid or a complex thereof with a metal ion.

(1) Publication number:

0 068 813 **A3** 

12

### **EUROPEAN PATENT APPLICATION**

(21) Application number: 82303281.8

22 Date of filing: 23.06.82

(5) Int. Cl.<sup>3</sup>: **C** .07 **F** 7/08 C .07 **F** 7/18, A 01 N 55/00

30 Priority: 24.06.81 US 276986 16.02.82 US 349261 12.05.82 US 377122

24.06.81 US 276987 16.02.82 US 349262

12.05.82 US 377121

- 43 Date of publication of application: 05.01.83 Bulletin 83/1
- B Date of deferred publication of search report: 16.03.83
- 84 Designated Contracting States: AT BE CH DE FR GB IT LI LU NL SE

- (1) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY **Legal Department 1007 Market Street** Wilmington Delaware 19898(US)
- (72) Inventor: Moberg, William Karl 1921 Kynwyd Road Wilmington Delaware 19810(US)
- (74) Representative: Hildyard, Edward Martin et al, Frank B. Dehn & Co. European Patent Attorneys Imperial House 15-19 Kingsway London WC2B 6UZ(GB)

- [54] Fungicidal 1,2,4-triazole and imidazole derivatives.
- (57) 1,2,4-Triazole and imidazole derivatives of the general

wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are alkyl, naphthyl or optionally substituted phenyl; or R2 and R3 may be hydroxy or alkoxy;

X is N, CH or CCH3; and

 $Q_1$  and  $Q_2$  are H or  $CH_3$ ;

are effective fungicides for controlling fungi in a plant locus. They may be formulated for use in conventional manner.

The compounds may be made e.g. by reacting a suitable chloromethylsilane with a suitable imidazole or 1,2,4-



## **EUROPEAN SEARCH REPORT**

EP 82 30 3281

	DOCUMENTS CONS	IDERED TO BE RELEVAN	T	
Category		h indication, where appropriate, rant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	FR-A-1 360 395 CORP.) *Page 12; cla example 3*	 (DOW CORNING ims 6,9; page 6,	2	C 07 F 7/08 C 07 F 7/18 A 01 N 55/00
A	FR-A-2 269 532 AG) *Page 13, claim	(DYNAMIT NOBEL	2	
A	23, 6th June 19 171534g, Columb V.D.SHELUDYAKOV sis of derivatives 3,5-dimethylpyr and benzimidaz	et al.: "Synthe- silicon-containing of azole, imidazole, ole" & ZH. OBSHCH.	2,16, 17	
	stract*	7(1), 90-6. *Ab-		TECHNICAL FIELDS SEARCHED (Int. Ci. 3)
D,A	US-A-3 692 798 *Column 5; clair	(SANDOR BARCZA)	2,15-	C 07 F 7/00
A	5, 5th February no. 29989a, Col & SU - A - 346	 CTS, vol. 78, no. 1973, page 523, umbus Ohio (USA); 306 (MIRONOV, V.F. 1972) *Abstract*	1,2	
	-			×
	The present search report has be	peen drawn up for all claims  Date of completion of the search	1	Examiner
<u> </u>	THE HAGUE	01-12-1982	SUTE	
CATEGORY OF CITED DOCUMENTS  X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document  CATEGORY OF CITED DOCUMENTS  T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filling date D: document cited in the application L: document cited for other reasons  A: member of the same patent family, corresponding document				

# This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

# **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:	
	☐ BLACK BORDERS
,	☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
	☐ FADED TEXT OR DRAWING
/	BLURRED OR ILLEGIBLE TEXT OR DRAWING
	☐ SKEWED/SLANTED IMAGES
	COLOR OR BLACK AND WHITE PHOTOGRAPHS
	☐ GRAY SCALE DOCUMENTS
	☐ LINES OR MARKS ON ORIGINAL DOCUMENT
	☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

# IMAGES ARE BEST AVAILABLE COPY.

**□** OTHER:

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.